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"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit.* lib. i. cap. 1. Not.

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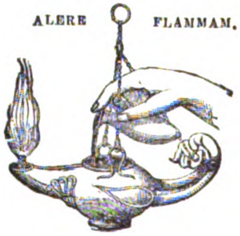
"Meditationis est perscrutari occulta; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

——"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.



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WITH FOUR PLATES.

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[SIXTH SERIES.]

JANUARY 1925.

I. *The Field of an Electron at Rest and in Uniform Motion.*

By H. Bateman (*California Institute of Technology*)*.

§ 1. *The Hypothetical Structure of an Electrostatic Field.*

WE shall assume that the usual ideas relating to the energy and momentum in an electromagnetic field hold good for the *simple radiant fields* in which the vectors E and H satisfy the relations

$$E^2=H^2, \quad (E.H)=0.$$

For the sake of generality, however, we shall multiply the usual expressions for energy and momentum by a constant factor λ which, later on, will be put equal to $\frac{1}{3}$.

In these fields, then, energy and momentum flow along straight lines with the velocity of light, the direction of flow at any point being that of the momentum. Dynamically the state of affairs may be compared with the free flight of a system of particles which do not influence one another and are not under the influence of external forces. We may, if we wish to adopt a reasonable hypothesis, speak of these particles as *quanta* †, but to be on safer ground we shall call them *field-atoms*.

More complicated electromagnetic fields may be obtained by superposing simple radiant fields *; for instance, if we differentiate with respect to z the components of E and H belonging to the simple radiant field

---

* Communicated by the Author.

† The idea of making quanta responsible for the energy and momentum of an electromagnetic field of this type and for the forces which it exerts may be regarded as due to Einstein. It was developed by Lorentz in his lectures at Pasadena.

$$\mathrm{H}_x = \frac{y}{x^2+y^2}, \qquad \mathrm{E}_x = -\frac{xz}{r(x^2+y^2)},$$

$$\mathrm{H}_y = -\frac{x}{x^2+y^2}, \qquad \mathrm{E}_y = -\frac{yz}{r(x^2+y^2)},$$

$$\mathrm{H}_z = 0 \quad , \qquad \mathrm{E}_z = \frac{1}{r},$$

we obtain the components of the field vectors for a point charge of electricity at the origin. The electrostatic field of a point charge may clearly be obtained in an infinite number of ways by superposing simple radiant fields, but it does not follow that it should be regarded as made up permanently of field-atoms, for the simple radiant fields may affect each other in some way—the field-atoms may collide and form *field-molecules*.

An attempt to obtain some information regarding the distribution of these hypothetical field-molecules will be based upon some rather crude analogies.

In the theory of light-quanta the number of s-fold light-quanta (light-molecules) of frequency ν in a cubic centimetre of cavity radiation is given by the formula of Wolfke †,

$$n_\nu^{(s)} = \frac{8\pi\nu^2}{sc^3} e^{-\frac{sh\nu}{\mathrm{RT}}}, \quad \ldots\ldots \quad (1)$$

where $n_\nu^s d\nu$ is the number whose frequencies lie between ν and $\nu + d\nu$. The associated density of energy is

$$u_\nu^{(s)} = \frac{8\pi h\nu^3}{c^3} e^{-\frac{sh\nu}{\mathrm{RT}}}. \quad \ldots\ldots \quad (2)$$

Denoting the energy $sh\nu$ of a light-molecule by U, the number of s-fold light-molecules whose energies lie between U and U $+ d$U is

$$n_{\mathrm{U}}^{(s)} = \frac{8\pi \mathrm{U}^2}{s(shc)^3} e^{-\frac{\mathrm{U}}{\mathrm{RT}}}, \quad \ldots\ldots \quad (3)$$

while the density of energy is

$$u_{\mathrm{U}}^{(s)} = \frac{8\pi \mathrm{U}^3}{s(shc)^3} e^{-\frac{\mathrm{U}}{\mathrm{RT}}}. \quad \ldots\ldots \quad (4)$$

The field-molecules at present under consideration are not necessarily light-molecules *, and we cannot speak of a temperature of an electrostatic field; but in the electrostatic field of an electron or proton there is a quantity, $\frac{e^2}{r}$, which has the same dimensions as RT, e being the charge on an electron; and so an attempt will be made to construct analogous formulæ in which RT is replaced by $\frac{\alpha e^2}{r}$, α being a constant which is at present undetermined.

---

* H. Bateman, Proc. London Math. Soc. (2) xviii. p. 95 (1919).

† M. Wolfke, *Phys. Zeitschr.* xxii. p. 375 (1921).

Since, in the theory of the Bohr atom of hydrogen, the kinetic energy of the revolving electron is $\frac{e^2}{2r}$, it seems possible that

$$\tfrac{3}{2}\mathrm{RT}=\frac{e^2}{2r}.$$

α would then be $\frac{1}{3}$. This guess may be wide of the mark.

Pursuing our analogy, we shall assume that the number of field-molecules with energy lying between U and U $+d$U in one cubic centimetre is

$$n_{\mathrm{U}}=k\mathrm{U}^2e^{-\frac{\mathrm{U}r}{\alpha e^2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where k is some unknown constant factor having the same physical dimensions as $(hc)^{-3}$. The density of energy which lies between U and U $+d$U is then †

$$\mathrm{W}_{\mathrm{U}}=k\mathrm{U}^3e^{-\frac{\mathrm{U}r}{\alpha e^2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and the total density of energy is

$$\mathrm{W}=k\int_0^\infty \mathrm{U}^3e^{-\frac{\mathrm{U}r}{\alpha e^2}}d\mathrm{U},$$

$$=6k\left(\frac{\alpha e^2}{r}\right)^4=6k\alpha^4e^6\,.\,\frac{e^2}{r^4}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The total number of field-molecules is, on the other hand ‡,

$$\mathrm{N}=k\int_0^\infty \mathrm{U}^2e^{-\frac{\mathrm{U}r}{\alpha e^2}}d\mathrm{U},$$

$$=2k\left(\frac{\alpha e^2}{r}\right)^3. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

---

* A calculation seems to indicate that light-atoms and light-molecules alone would not give a sufficiently high value of the density of energy. A field-molecule is supposed to have stationary mass.

† The calculation mentioned in the last footnote is based on the supposition that $k=\frac{8\pi}{(hc)^3}\sum_1^\infty\frac{1}{s^4}$ and $\alpha=\frac{1}{3}$.

‡ This law is practically the same as one used in a previous attempt to determine the structure of an electrostatic field. 'Publications of the Astronomical Society of the Pacific,' April 1922.

If we suppose that a certain percentage of these are moving outwardly in a radial direction with some velocity v which is the same for all the molecules of this set, the rate at which these molecules diminish in number owing to collisions is proportional to

$$-\frac{1}{r^2}\frac{d}{dr}\left[2k\frac{\alpha^3 e^6}{r}\right] = \frac{2k}{r^4}\alpha^3 e^6 ;$$

it is thus proportional to the density of energy, and we have a law analogous to the law of mass action. On account of the inverse cube law, the number of field molecules of this type that go to infinity is zero.

If this hypothesis is correct, there is some mechanism in an electrostatic field which prevents the field entities from completely leaving the neighbourhood of the charge. Electromagnetic theory itself suggests that this may be the case, for the coordinated motion of the set of point charges constituting an electron of finite size appears in simple cases, such as that of uniform motion, to be of such a nature that lines of force issuing from different point charges are permanently incident [*]. Now it may be legitimate to regard the lines of force of a point charge as made up of field-atoms or molecules travelling with the velocity of light along straight lines [†]; but the theorem just mentioned suggests that the structure of the electron is of such a nature that the emitted field-atoms (molecules) collide sooner or later, and it seems reasonable, then, to suppose that the electron uses the same entities over and over again in producing its field, so long as it is in uniform motion and free from the influence of external fields.

It may be possible to carry our analogy further, and to suppose that at any fixed distance r from the centre of an electron there is a condition analogous to that of thermal equilibrium. The work of Pauli [‡] and Bothe [§] on thermal equilibrium between electrons and light-quanta can be extended perhaps to the present problem if it is assumed that the number of field-molecules with stationary mass lying between M and M$+d$M, and component momenta lying between (G_x, G_y, G_z) and $(G_x+dG_x, G_y+dG_y, G_z+dG_z)$ is proportional to

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[*] H. Bateman, *l. c.*

[†] Leigh Page, Amer. J. Science, xxxviii. p. 169 (1914); H. Bateman, *l. c.* The field-atoms may move either towards or away from the charge.

[‡] W. Pauli, *Zeitschr. f. Phys.* xviii. p. 272 (1923).

[§] W. Bothe, *ibid.* xxiii. (1924).

$$e^{-\frac{Ur}{ac^2}}dG_x dG_y dG_z f(M)dM, \quad . \quad . \quad . \quad . \quad (9)$$

the factor being a function of M. This is a simple generalization of Maxwell's law and of the equation adopted by Pauli[*] and Bothe[†]. It is not certain that this hypothesis is compatible with (6), and it is likely that a more general form will be needed if the stationary mass of a field-molecule can alter in a collision. The hypothesis makes the total momentum per unit volume equal to zero, and the supposition of a type of thermal equilibrium at the distance r seems to require that there should be no transverse flow of momentum and, in fact, that the field should be entirely free from stress. Indeed an unbalanced pressure depending on r would give rise to a body force in the field. The pressure of the field-molecules must be balanced by forces between them. A residual pressure or tension which is constant throughout space is quite compatible with the present ideas, but we are interested at present in the departure from uniform normal stress when we speak of stresses in the field. In this sense, then, we may conclude that the field is free from stress. This conclusion should hold whether equation (9) needs alteration or not, and must now be discussed.

In the classical electromagnetic theory there are stresses even in the field of an isolated electric charge, and their existence is supposed to be confirmed by the existence of a stress at the surface of a charged conductor or soap-bubble; but in the case of an electron the supposed existence of such a stress presents a difficulty, as the electron might be expected to blow up. If, on the other hand, we adopt the above idea that the electrostatic field of an electron is entirely free from stress, some modification must be made in the specification of the state of stress in an electromagnetic field. A possible modification has already been suggested but not definitely adopted[‡], and will now be presented in a more complete form.

§ 2. *Energy, Momentum, and Stresses in the Field of an Electron in Uniform Motion.*

Using W to denote the density of energy, (S_x, S_y, S_z) to denote the components of the flow of energy, (G_x, G_y, G_z) for the components of the density of momentum, and X_x, X_y, X_z; Y_x, Y_y, Y_z; Z_x, Z_y, Z_z for the components of stress, we assume that

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[*] W. Pauli, *l. c.*

[†] W. Bothe, *l. c.*

[‡] Mess. of Math. lii. p. 116 (1922); 'Science,' lvii. p. 238 (1923). The calculations in the first paper are made with a slightly different tensor, but the present one is mentioned as suitable.

$$3X_x = E_x^2 + H_x^2 - \tfrac{1}{2}(E^2+H^2) - 2\Psi\frac{\partial^2\Psi}{\partial x^2} + \Gamma + \frac{\partial^2\Omega}{\partial x^2} - \Box\Omega,$$

$$3X_y = E_xE_y + H_xH_y - 2\Psi\frac{\partial^2\Psi}{\partial x\partial y} + \frac{\partial^2\Omega}{\partial x\partial y} = 3Y_x,$$

$$3W = \tfrac{1}{2}(E^2+H^2) + \frac{2}{c^2}\Psi\frac{\partial^2\Psi}{\partial t^2} + \Gamma - \frac{1}{c^2}\frac{\partial^2\Omega}{\partial t^2} - \Box\Omega,$$

$$3S_x = c(E_yH_z - E_zH_y) - 2\Psi\frac{\partial^2\Psi}{\partial x\partial t} + \frac{\partial^2\Omega}{\partial x\partial t} = 3c^2G_x,$$

. . . .

where

$$\Gamma = \left(\frac{\partial\Psi}{\partial x}\right)^2 + \left(\frac{\partial\Psi}{\partial y}\right)^2 + \left(\frac{\partial\Psi}{\partial z}\right)^2 - \frac{1}{c^2}\left(\frac{\partial\Psi}{\partial t}\right)^2,$$

$$\Omega = \tfrac{5}{8}\Psi^2,$$

and

$$\Box\Omega \equiv \frac{\partial^2\Omega}{\partial x^2} + \frac{\partial^2\Omega}{\partial y^2} + \frac{\partial^2\Omega}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2\Omega}{\partial t^2}.$$

In these equations (E_x, E_y, E_z), (H_x, H_y, H_z) denote the components of electromagnetic field vectors that are calculated from the volume density ρ and velocity v of the electricity by means of the usual formulæ

$$H = \text{curl } A, \qquad E = -\frac{1}{c}\frac{\partial A}{\partial t} - \nabla\Phi,$$

$$\Phi = \frac{1}{4\pi}\iiint\frac{d\xi d\eta d\zeta}{r}[\rho]_{\xi,\eta,\zeta},$$

$$A = \frac{1}{4\pi c}\iiint\frac{d\xi d\eta d\zeta}{r}[\rho v]_{\xi,\eta,\zeta},$$

$$r^2 = (x-\xi)^2 + (y-\eta)^2 + (z-\zeta)^2 = c^2(t-\tau)^2, \quad (\tau \leqq t),$$

and Ψ is a scalar potential which is invariant under the transformations of the theory of relativity (for uniform motions), and is given by the formula

$$\Psi = \frac{1}{4\pi}\iiint\frac{d\xi d\eta d\zeta}{r}\left[\rho\sqrt{1-\frac{v^2}{c^2}}\right]_{\xi,\eta,\zeta}.$$

Outside the electron we have $\Box\Psi=0$, and so the equations

$$\left.\begin{aligned} \operatorname{div} X - \frac{\partial G_x}{\partial t} &= 0, \\ \operatorname{div} S + \frac{\partial W}{\partial t} &= 0, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

which express the principles of the conservation of momentum and energy, are seen to be satisfied.

When the electron is stationary we may write

$$\Psi=\Phi=\frac{\sigma}{r},$$

where $4\pi\sigma=e$, the charge on the electron. We have then

$$\Gamma=\frac{\sigma^2}{r^4}, \qquad \Box\Omega=\frac{5\sigma^2}{4r^4}, \qquad \frac{\partial^2\Omega}{\partial x^2}=\frac{5\sigma^2x^2}{r^6}-\frac{5\sigma^2}{4r^4},$$

$$E_x^2-\tfrac{1}{2}E^2=\frac{\sigma^2x^2}{r^6}-\frac{\sigma^2}{2r^4}, \qquad 2\Psi\frac{\partial^2\Psi}{\partial x^2}=-\frac{2\sigma^2}{r^4}+\frac{6\sigma^2x^2}{r^6},$$

$$X_x=X_y=S_x=0, \qquad W=\frac{\sigma^2}{12r^4}.$$

Thus there is no momentum and no flow of energy. The space outside the electron is entirely free from stress.

Equating the present value of W to that obtained in § 1, we have

$$6k\alpha^4e^6=\frac{1}{12(4\pi)^2}.$$

The presence of the factor 3 in the expressions for X_x etc. may puzzle the reader at first, but the explanation is * that in the present theory one-third of the electric force arises from the field vectors E and H, while the other two-thirds arises from the scalar potential Ψ.

The expressions for X_x etc. have been constructed so that they will transform in the standard way in a relativity transformation †.

Passing to the case of uniform motion with the aid of the relativity transformation,

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* *L. c.* This cannot be regarded as definitely proved.

† Dr. Silberstein has mentioned to me in a letter that this point ought to be emphasized. The terms depending on Ω are analogous to those considered by E. Furlanetto in a solution of the problem of Morera (*Nuovo Cimento*, xvi. p. 139, 1918).

$$x=\beta(x'-vt'), \quad t=\beta\left(t'-\frac{vx'}{c^2}\right), \quad y=y', \quad z=z',$$

$$\beta=\frac{1}{\sqrt{1-\frac{v^2}{c^2}}},$$

we find with the aid of the invariant relation

$$\begin{aligned} X_x dx^2 + X_y dy^2 + X_z dz^2 + 2Y_z dy\,dz + 2Z_x dz\,dx + 2X_y dx\,dy \\ + 2S_x dx\,dt + 2S_y dy\,dt + 2S_z dz\,dt - c^2 W dt^2 = X_x' dx'^2 + \ldots \\ \ldots\ldots \quad - c^2 W' dt'^2, \end{aligned}$$

that

$$W'=\beta^2 W, \qquad S_x'=c^2 G_x'=v\beta^2 W,$$

$$X_x'=-\frac{v^2}{c^2}\beta^2 W, \qquad X_y'=X_z'=0,$$

$$Y_z'=Y_y'=Z_z'=S_y'=S_z'=0.$$

Hence the momentum is parallel to the axis of x, and is $\mu' v$, where the mass density μ' is given by

$$\mu'=\frac{W'}{c^2}.$$

The energy and momentum, moreover, flow with velocity v in the direction of the axis of x. Our tensor, $X_x' \ldots W'$, thus satisfies the conditions that many physicists have secretly thought[*] ought to be satisfied by a tensor which correctly represents the state of affairs outside the electron. It should be noticed also that W' is positive, X_x' negative, and $S_x'^2 < W^2$; it is quite possible, then, for the densities of energy and momentum and the flow of momentum to be produced by moving field-atoms or field-molecules[†].

By limiting our expressions for $X_x \ldots W$ to the case of the uniform motion of an electron, we avoid the difficulty that negative values of W appear in some places when an attempt is made to apply this tensor as it stands to the case of accelerated motion of an electron. That either the tensor or the field needs modification in this case appears also from the circumstance that the formula for the force between two electrons in relative motion is not quite right.

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[*] Judging from a conversation with Drs. Lorentz and Epstein.

[†] In making this remark, I must acknowledge my indebtedness to some investigations of Einstein and Lorentz which emphasize the importance of these inequalities, which are well known in kinetic theory.

§ 3. *The Interior of the Electron.*

For the interior of the electron the expressions for X_x etc. need modification, for the density of energy should be positive and the stress should vanish at the boundary when the electron is at rest. These conditions may be satisfied by adding to the former expressions for $X_x \ldots$ additional terms $X_x{}^a \ldots$, given by

$$3X_x{}^a = -2\omega\Psi_a - 2\Psi_a\beta\rho\frac{v_x{}^2}{c^2},$$

$$3X_y{}^a = -2\Psi_a\beta\rho\frac{v_x v_y}{c^2},$$

$$3W^a = -2\omega\Psi_a + 2\Psi_a\beta\rho,$$

$$3S_x{}^a = 2\Psi_a\beta\rho v_x,$$

where $\beta = \dfrac{1}{\sqrt{1-\dfrac{v^2}{c^2}}}$, and where Ψ_a and ω are the values of Ψ and $\rho\sqrt{1-\dfrac{v^2}{c^2}}$ at the boundary of the electron, these values being supposed constant over the boundary. The conditions may be satisfied in another way by replacing the quantities β, ρ, v in the foregoing expressions by their constant boundary values. This eliminates the last term in the ensuing expression for W and gives the usual expression for the total energy of an electrostatic field. The present calculations are made with the expressions given in the text, but it must be acknowledged that the alternate solution has some advantages.

When the electron is stationary we may write $\Psi = f(r)$. Using primes to denote differentiations with respect to r, we have now

$$\frac{\partial^2\Psi}{\partial x^3} = \frac{x^2}{r^2}f'' + \frac{1}{r}f' - \frac{x^2}{r^3}f',$$

$$\frac{\partial^2\Omega}{\partial x^2} - \Box\Omega = -\frac{4}{r}ff' - \frac{y^2+z^2}{r^2}\left[2f'^2 + 2ff'' - \frac{2ff'}{r}\right].$$

At the point $x=a$, $y=0$, $z=0$ on the spherical boundary $r=a$, Ψ and Ψ' are continuous, consequently $f\,.\,f'$, $\dfrac{\partial^2\Psi}{\partial x\,\partial y}$, $\dfrac{\partial^2\Psi}{\partial x\,\partial z}$, and $\dfrac{\partial^2\Omega}{\partial x^3} - \Box\Omega$ are continuous, but the discontinuity in $\dfrac{\partial^2\Psi}{\partial x^2}$ is $-\omega$ and is just sufficient to make $-2\omega\Psi_a - 2\Psi\dfrac{\partial^2\Psi}{\partial x^2}$

continuous. Hence the stresses X_x, X_y, X_z are all continuous at the boundary and are consequently zero. Turning the axes round, we see that *the boundary of the electron is entirely free from stress.*

Inside the electron

$$W = \tfrac{1}{12} f'^2 + \tfrac{5}{12} \rho f + \tfrac{2}{3} \Psi_a (\rho - \rho_a).$$

Now the law of variation of ρ with r is determined by equations (10), which give

$$\rho \Psi' = 2 \Psi \rho',$$

or $\Psi = b\rho^2$, where ρ is a constant. Since Ψ is the electrostatic potential derived from ρ, we write

$$\rho = A_0 + A_2 r^2 + A_4 r^4 + \ldots,$$

$$\Psi = \frac{A_0}{6}(3a^2 - r^2) + \frac{A_2}{20}(5a^4 - r^4) + \frac{A_4}{42}(7a^6 - r^6) + \ldots,$$

and find that

$$\rho = A_0 \left[1 - \frac{s}{12}\left(\frac{r}{a}\right)^2 - \frac{s^2}{720}\left(\frac{r}{a}\right)^4 - \ldots \right]$$

where $s = \dfrac{a^2}{A_0 b}$ is given by the equation

$$0 = 1 - \tfrac{1}{2} s + \tfrac{1}{48} s^2 + \ldots - .$$

This equation for s appears to have two positive roots, the smaller of which is approximately

$$s = 2{\cdot}209012572.$$

It may be proved that the series for ρ converges when s has this value.

With either root of this equation, $|\rho|$ decreases from a maximum value at the centre of the electron to a smaller value $|\rho_a|$ at the boundary; also Ψ and ρ evidently have the same sign, and so ρf and $\Psi_a(\rho - \rho_a)$ are both positive.

Hence W is everywhere positive.

The mass m of the electron, when calculated from its total energy, is given by

$$mc^2 = 4\pi \int_0^a \left[\frac{1}{12} f'^2 - \frac{5}{12} f\left(f'' + \frac{2}{r} f' \right) + \frac{2}{3} \Psi_a (\rho - \rho_a) \right] r^2 \, dr$$

$$+ \frac{4\pi\sigma^2}{12} \int_a^\infty \frac{dr}{r^2}$$

$$= 4\pi \left[\frac{1}{4} r^2 f f' + \frac{1}{6} r^3 f'^2 + \frac{2}{9} r^3 f'^{3/2} b^{-1/2} - \frac{2}{3} r^2 f' \Psi_a \right.$$

$$\left. - \frac{2}{9} r^3 \rho_a \Psi_a \right]_0^a + \frac{\pi\sigma^2}{3a}$$

$$= \frac{8\pi\sigma^2}{3a} = \frac{e^2}{6\pi a}.$$

Hence the mass of the electron is the same as that of a Lorentzian electron with uniform surface charge. The same result is obtained when the mass is calculated from the momentum of the electron in uniform motion[*]. A calculation shows that the new electron is stable for radial displacements in which the electricity acts as an incompressible and inextensible fluid.

The fact that the present analysis does not indicate the size of the electron need not trouble us, because the radius of an electron must be expressed in terms of something else and at present there is no other length available. When the problem of the motion round a nucleus of an electron of finite size has been solved, it will be possible to compare the radius of an electron with its distance from the nucleus. In Einstein's theory of gravitation the size of the electron is supposed to be determined by the curvature of the world.

§ 4. *Further Remarks on Collisions between Field-atoms.*

In § 1 it is supposed that two field-atoms may combine to form a field-molecule with a stationary mass which may be different from zero. Now, if the field-atoms are light-quanta, the question may be asked why field-molecules do not exist to any appreciable extent in cavity radiation. The explanation may be that in cavity radiation a light-quantum is orientated at right angles to its direction of motion[†], while in an electrostatic field this may not be the case. The nature of a collision between two light-quanta may very well depend upon their orientations[‡], especially if light-quanta are

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[*] This depends on the fact that the mean value of X_x over the stationary electron is zero.

[†] According to Emden (*Phys. Zeitschr.* xxii. p. 513, 1921), a light-quantum has 6 degrees of freedom, and so we can speak of its orientation.

[‡] Dr. Tolman has also had in mind the possibility of two light-quanta describing orbits round each other under certain circumstances and sticking together, so to speak. The idea of light condensing into some form of matter is used by Sir Oliver Lodge (Phil. Mag. xli. p. 549, 1921) and by W. D. Macmillan in several articles; it is probably a very old idea. The idea seems to imply that a light-quantum has an appreciable influence on the space-time metric. In this connexion it may be mentioned that an interval ds satisfying Einstein's gravitational equations and representing a mass travelling with uniform velocity c has been found to be given by

$$ds^2=c^2dt^2-dx^2-dy^2-dz^2+f(x-ct, y, z)(dx-cdt)^2,$$

where $\frac{\partial^2 f}{\partial y^2}+\frac{\partial^2 f}{\partial z^2}=0$ outside the moving mass. The idea that light produces a deformation of space but not of time is used by F. Famà, 'Le radiazioni energetiche,' Bologna, 1921; it must naturally lead to a different result. The formula just mentioned has been confirmed by Mr. H. P. Robertson, it was suggested by a result obtained by the author in 1910 (Proc. Lond. Math. Soc. (2) vol. x. p. 7).

analogous to electric dipoles. Furthermore, at a sufficient distance from the boundary the number of field-molecules per c.c. arising from the electrical fields of the material particles will be negligible in comparison with the number of quanta.

To make this difference in orientation seem plausible, let us consider the generation of a line of electric force by emitted field-entities that travel without colliding. If the motion of the point charge is uniform and rectilinear, the direction of projection of the entities does not vary, and so the line joining two entities, emitted at successive instants, keeps one direction and never becomes perpendicular to its direction of motion. When, however, the motion of the point charge of electricity is accelerated in any manner, the direction of projection of successive entities is not the same, and the line joining these entities varies during their motion and becomes eventually almost perpendicular to their directions of motion. This corresponds more nearly to the case of the light-quantum.

A collision between two light-quanta of energies $h\nu$ and $h\nu'$ respectively may be treated very simply with the aid of the principles of the conservation of energy and momentum.

Assuming that the quanta combine to form a field-molecule of mass m moving with velocity v, we have the equations

$$\left.\begin{aligned} h\nu + h\nu' &= mc^2\beta, \\ h\nu\, l + h\nu'\, l' &= mc\beta v_x, \\ h\nu\, m + h\nu'\, m' &= mc\beta v_y, \\ h\nu\, n + h\nu'\, n' &= mc\beta v_z, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where

$$\beta = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$$

and (l, m, n), (l', m', n') are the direction cosines of the lines of motion of the quanta. Drawing lines OA . OB of length c in the direction of these two lines of motion, the velocity v is represented by OV, where V divides AB so that

$$\nu \,.\, \mathrm{VA} = \nu'\, \mathrm{BV}.$$

Similar equations hold when a field-molecule breaks up into two light-quanta.

It should be remarked that collisions between light-quanta which result in the formation of an exceedingly short-lived field-molecule are quite compatible with the permanence of cavity radiation, for the existence of the field-molecules may then be ignored. A collision between two light-quanta may, in fact, be supposed to result simply in changes in direction and energy of the quanta that conserve energy and momentum.

Formula (1) indicates that the number of s-fold quanta whose frequencies belong to the interval $(\nu, \nu+d\nu)$ and whose directions belong to the solid angle $d\omega$ is

$$\frac{2\nu^2}{sc^3} e^{-\frac{sh\nu}{RT}} d\nu\, d\omega\, ;$$

hence the number of such quanta whose momenta belong to the region $dG_x\, dG_y\, dG_z$ is

$$N = \frac{2}{s^4 h^3} e^{-\frac{U}{RT}} dG_x\, dG_y\, dG_z,$$

where $U = sh\nu$ is the energy of an s-fold quantum of frequency ν.

Now the chance that a definite s-fold quantum, which belongs to the momentum region $dG = dG_x\, dG_y\, dG_z$, may hit an l-fold quantum $lh\mu$ of frequency μ belonging to the region of momentum $d\Gamma$ in the interval of time dt and produce a deflexion which, in the system of normal coordinates of Pauli is represented by a line contained in the solid angle $d\Omega_0$, is

$$NK\, u_\mu{}^l\, d\Gamma\, d\Omega_0\, dt = \frac{2}{s^4 h^3} K e^{-\frac{U}{RT}} u_\mu{}^l\, dG\, d\Gamma\, d\Omega_0\, dt,$$

where K is a factor which, according to the investigation of Pauli, is of the form

$$K = \frac{\chi}{E^4 U},$$

where $E = lh\mu$ and χ is invariant under a Lorentz transformation. This quantity χ depends on the states of the initial and final quanta.

Let the final quanta be $s_1 h\nu_1$ and $l_1 h\mu_1$ of energies U_1, E_1 respectively, and suppose that they belong to the regions of momentum dG_1, $d\Gamma_1$ respectively, then we have Pauli's relation

$$\frac{dG\, d\Gamma}{UE} = \frac{dG_1\, d\Gamma_1}{U_1 E_1}.$$

In equilibrium the direct process will occur just as often as the inverse. The condition for this is

$$\frac{2}{s^4 h^3} K e^{-\frac{U}{RT}} u_\mu{}^l \, dG \, d\Gamma \, d\Omega_0 = \frac{2}{s_1{}^4 h^3} K_1 e^{-\frac{U}{RT}} u_{\mu_1}{}^{l_1} \, dG_1 \, d\Gamma_1 \, d\Omega_0 .$$

Substituting the values

$$u_\mu{}^l = \frac{8\pi h \mu^3}{c^3} e^{-\frac{lh\mu}{RT}}, \qquad u_{\mu_1}{}^{l_1} = \frac{8\pi h \mu_1{}^3}{c^3} e^{-\frac{l_1 h \mu_1}{RT}},$$

and making use of the relation

$$U + lh\mu = U_1 + l_1 h \mu_1,$$

we find that

$$\frac{\chi}{s^4 l^3} = \frac{\chi_1}{s_1{}^4 l_1{}^3}.$$

This indicates that the ratio $\chi : \chi_1$ is independent of T, and so equilibrium is possible.

Equations (11) are very similar to some equations which govern the directions of projection of electric dipoles projected from a primary singular point moving with velocity v, the radiant field being specified by simple expressions * when the directions of projection are related in this way.

The interpretation which was subsequently given to the equations just mentioned is as follows:—

Consider two particles P and Q moving with velocities less than c along two curves, C and Γ, which are very close together.

A particle travelling with the velocity of light runs backwards and forwards from P to Q. Let $P_1Q_1P_2Q_2 \ldots$ be the zigzag path of this particle, $\boldsymbol{v}$ the velocity of P; then the direction cosines (l, m, n), (l', m', n') of the lines P_1Q_1, Q_1P_2 are connected approximately by the equations

$$\left.\begin{aligned} c\tau l + c\tau' l' &= v_x(\tau + \tau'), \\ c\tau m + c\tau' m' &= v_y(\tau + \tau'), \\ c\tau n + c\tau' n' &= v_z(\tau + \tau'), \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (12)$$

where τ is the time from P_1 to Q_1, and τ' the time from Q_1 to P_2. These equations are the same as (11) if

$$\nu\tau' = \nu'\tau.$$

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* See the expressions for the potentials in Phil. Mag. Oct. 1913, p. 581, which hold when the directions of projection are related in the present way, and not only in the particular way assumed then.

This means that the frequency ν' is inversely proportional to τ, and the frequency ν to τ'. Regarding ν as approximately the frequency of a field-atom emitted in the direction P_2Q_2, we notice that this frequency is inversely proportional to the length of the interval of time between the successive collisions at Q_1 and P_2.

The equations (12) also occur in the theory of the lines of electric force of a moving electric pole when a line of force is supposed to be made up of particles travelling along straight lines with velocity c and emitted in directions whose direction cosines (l, m, n) vary with the velocity v of the pole in a manner specified by the equations

$$(c^2-v^2)\frac{dl}{dt} = (v_x-cl)\left(l\frac{dv_x}{dt}+m\frac{dv_y}{dt}+n\frac{dv_z}{dt}\right) + \frac{dv_x}{dt}(c-lv_x-mv_y-nv_z) \quad . \quad . \quad . \quad . \quad (13)$$

. . . .

Murnaghan has shown* that if (l, m, n) satisfy these equations, then (l', m', n) also satisfy them, l, m, n, l', m', n' being connected by equations of type (12).

§ 5. *Generalized Parallelism and the Equations of Motion of an Electron.*

If some generalization of the theory of § 2 is correct, the equations of motion of an electron need modification, and so it seems worth while to consider some possibilities, using Einstein's theory of gravitation as a guide.

The idea of the path of a particle as a geodesic in a Riemann space is closely connected with Levi Civita's idea of motion by parallelism †, a geodesic being a curve whose tangents are all parallel in the sense of Levi Civita. The idea of a geodesic may be generalized, then, by generalizing the idea of parallelism.

One generalization has already been given by J. Lipka ‡, who has introduced the idea of conformal parallelism. Another generalization, which will be more useful for our purpose, is suggested by the equations (13), or rather the four-dimensional form of these equations.

Using the notation of Einstein's theory, a contravariant vector $\xi^{(n)}$ will be said to move parallel to itself along a curve C whose element of interval is ds if the components of the vector vary along the curve in a manner specified by the differential equations

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* Amer. Journ. Math. April 1917.

† *Rend. Palermo*, xlii. p. 1 (1917).

‡ 'Publications of the Massachusetts Institute of Technology,' II. June 1923.

$$\frac{d\xi^{(n)}}{ds} + \begin{Bmatrix} lm \\ n \end{Bmatrix} \frac{dx^{(l)}}{ds} \xi^{(m)} + g^{(nr)} p_r + g^{(nr)} a_{rm} \xi^{(m)} - \xi^{(n)} p_r \xi^{(r)} = 0,$$

where p_r is a covariant vector, g_{mn} a symmetric and a_{rm} an antisymmetric covariant tensor, and $\begin{Bmatrix} lm \\ n \end{Bmatrix}$ is the Christoffel symbol derived from g_{mn}. The quantities g_{mn}, a_{rm}, and p_r may be supposed to specify the gravitational field and the electromagnetic vector and scalar fields. The contravariant tensor $g^{(nr)}$ is supposed to be derived from g_{mn} in the usual way.

These equations are compatible with the equation

$$g_{mn} \xi^{(m)} \xi^{(n)} = 1 ;$$

and so we may apply them in particular to the contravariant vector

$$\xi^{(n)} = \frac{dx^{(n)}}{ds}$$

if ds is defined by means of the equation

$$ds^2 = g_{mn}\, dx^{(m)}\, dx^{(n)}.$$

The resulting equations[*],

$$\frac{d^2x^{(n)}}{ds^2} + \begin{Bmatrix} lm \\ n \end{Bmatrix} \frac{dx^{(l)}}{ds} \frac{dx^{(m)}}{ds} + g^{(nr)} p_r + g^{(nr)} a_{rm} \frac{dx^{(m)}}{ds} - \frac{dx^{(n)}}{ds} p_r \frac{dx^{(r)}}{ds} = 0,$$

will be studied as possible equations of motion of an electron; and to simplify the discussion, we shall consider only the simple case in which

$$ds^2 = c^2dt^2 - dx^2 - dy^2 - dz^2.$$

In order to obtain a definite case for discussion, we shall assume that p_n is the gradient of a scalar invariant Ψ, and shall write our equations of motion in the form:

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[*] These equations resemble in some respects the equations of motion considered by L. P. Eisenhart, Annals of Math. xxiv. p. 367 (1923).

$$\frac{d}{dt}\left[\frac{mv_x}{\sqrt{1-\frac{v^2}{c^2}}}\right]=\frac{1}{3}e\left[E_x+\frac{1}{c}(v_yH_z-v_zH_y)\right]$$

$$-\frac{2}{3}e\sqrt{1-\frac{v^2}{c^2}}\frac{\partial\Psi}{\partial x}-\frac{2}{3}\frac{e}{c^2}\frac{v_x}{\sqrt{1-\frac{v^2}{c^2}}}\frac{\partial\Psi}{\partial t},$$

. . . .

$$\frac{d}{dt}\left[\frac{mc^2}{\sqrt{1-\frac{v^2}{c^2}}}\right]=\frac{1}{3}e\left[v_xE_x+v_yE_y+v_zE_z\right]$$

$$+\frac{2}{3}e\sqrt{1-\frac{v^2}{c^2}}\frac{\partial\Psi}{\partial t}-\frac{2}{3}\frac{e}{\sqrt{1-\frac{v^2}{c^2}}}\frac{d\Psi}{dt},$$

where m is the stationary mass, e the charge, and (v_x, v_y, v_z) the component velocities of the electron, while

$$\frac{d}{dt}=\frac{\partial}{\partial t}+v_x\frac{\partial}{\partial x}+v_y\frac{\partial}{\partial y}+v_z\frac{\partial}{\partial z},$$

$$v^2=v_x^2+v_y^2+v_z^2.$$

These equations have been chosen because they were suggested by, but not rigorously derived from, the electromagnetic theory of § 2. They evidently need some modification because $e\sqrt{1-\frac{v^2}{c^2}}\frac{\partial\Psi}{\partial x}$ is not quite the same as $e\left[E_x+\frac{1}{c}(v_yH_z-v_zH_y)\right]$, although in simple cases the difference between the two is negligible. The equations have been thought to be worth discussing because in the most important case they are readily integrable.

Assuming that the electron moves in the field of a stationary nucleus of charge $-e$, we write

$$E=-\nabla\Psi,\qquad \Psi=-\frac{e}{r},\qquad H=0.$$

Transforming to polar coordinates, we have the equation

$$\frac{m}{\sqrt{1-\frac{v^2}{c^2}}}(r\ddot{\theta}+2\dot{r}\dot{\theta})+\frac{mv\dot{v}r\dot{\theta}}{c^2\left(1-\frac{v^2}{c^2}\right)^{3/2}}=-\frac{2e^2}{3c^2}\frac{\dot{r}\dot{\theta}}{r\sqrt{1-\frac{v^2}{c^2}}}$$

for the variation of angular momentum. Writing this equation in the form

$$m\frac{d}{du}\left(\frac{r^2\dot{\theta}}{\sqrt{1-\frac{v^2}{c^2}}}\right)=\frac{2e^2}{3c^2}\frac{r^2\dot{\theta}}{\sqrt{1-\frac{v^2}{c^2}}},$$

where $u=\frac{1}{r}$, we have the first integral

$$\frac{r^2\dot{\theta}}{\sqrt{1-\frac{v^2}{c^2}}}=Ac\,\epsilon^{au}, \qquad a=\frac{2e^2}{3c^2m}, \qquad . \quad . \quad (14)$$

where A is an arbitrary constant.

A second integral may be obtained from the energy equation

$$\frac{d}{dt}\left(\frac{mc^2}{\sqrt{1-\frac{v^2}{c^2}}}\right)=-\frac{e^2\dot{r}}{3r^2}\left(1+\frac{2}{\sqrt{1-\frac{v^2}{c^2}}}\right),$$

and we find that

$$1+\frac{2}{\sqrt{1-\frac{v^2}{c^2}}}=B\epsilon^{au},$$

where B is a second arbitrary constant.

Writing

$$v^2=\dot{r}^2+r^2\dot{\theta}^2,$$

and solving for $\frac{d\theta}{du}$, we find eventually that

$$\theta=2A\int\frac{\epsilon^{au}\,du}{\sqrt{(B\epsilon^{au}-1)^2-4(1+A^2u^2\epsilon^{2au})}}.$$

When A and B are chosen arbitrarily, the equation in u,

$$(B\epsilon^{au}-1)^2-4(1+A^2u^2\epsilon^{2au})=0,$$

has its smallest positive root as a simple root, and the orbit has an apse at the corresponding value of u; but when the equation has two equal positive roots, the orbit approaches a circle asymptotically. Thus an electron can gradually settle down into a circular orbit, or it can gradually get out *, but of course it will take an infinite time for it to get out. The present theory does not give any indication of quantum conditions, but in the author's opinion these may be connected in some way with the equilibrium of the electronic structure in an orbital motion.

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* I am indebted to Mr. R. M. Langer for the remark that it can get out.

II. *Theory of the Condenser in a New Electrostatics.* *By* H. BATEMAN (*California Institute of Technology*) *.

§ 1. *The Distribution of Stress in an Electrostatic Field.*

IT has been shown recently that, by adopting a new tensor for the specification of the distribution of stress, momentum, and energy in the field of an electron in uniform rectilinear motion, it is possible to account for the existence of discrete electrons with a volume distribution of electricity of one sign, the electricity being everywhere in equilibrium.

In the electrostatic case, when the electron is at rest relative to the axes of coordinates, the tensor takes a simpler form because the retarded potential ψ, which is an invariant for the transformations of the restricted theory of relativity, then becomes equal to the electrostatic potential ϕ. In this case we have in the usual notation †,

$$\left.\begin{aligned} X_x &= \tfrac{3}{4}\left(\frac{\partial\phi}{\partial x}\right)^2 - \tfrac{1}{4}\phi\frac{\partial^2\phi}{\partial x^2} - \tfrac{1}{4}R^2 + \tfrac{5}{12}\phi\rho - p, \\ X_y &= \tfrac{3}{4}\frac{\partial\phi}{\partial x}\frac{\partial\phi}{\partial y} - \tfrac{1}{4}\phi\frac{\partial^2\phi}{\partial x\partial y} = Y_x, \end{aligned}\right\} \quad . \quad . \quad (1)$$

where ρ is the density of electricity and p a constant which is zero in the æther and different from zero inside the electric charges. The quantity R^2 is defined by

$$R^2 = \left(\frac{\partial\phi}{\partial x}\right)^2 + \left(\frac{\partial\phi}{\partial y}\right)^2 + \left(\frac{\partial\phi}{\partial z}\right)^2,$$

and the associated density of energy is

$$W = \tfrac{1}{12}R^2 + \tfrac{5}{12}\phi\rho.$$

When $\phi = \dfrac{1}{r}$ the components of stress in the æther vanish completely, and so in the present theory the space outside a stationary spherical electron is entirely free from stress. If ϕ is a solution of Laplace's equation we have

$$\text{div.}\,X = 0, \quad \text{div.}\,Y = 0, \quad \text{div.}\,Z = 0,$$

and so the stress distribution for the æther seems likely to be a possible one for an electrostatic field of a more general character. In endeavouring to apply this stress-distribution to problems of electrostatics we must remember that in these problems the electricity is not free but is associated with matter, consequently the stress-distribution in regions of space occupied by electricity will not generally be that specified by (1), for the matter exerts forces on the electricity and will give rise to an additional distribution of stress in the electric layer.

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* Communicated by the Author.

† The tensor adopted here is that suggested at the top of p. 126 of my paper, "Electromagnetism and Dynamics," Mess. of Math. lii. (1922), except that each component has been divided by three, and a constant mass-tensor is used in place of the variable one.

§ 2. *The Electrified Soap Bubble.*

In a region occupied by electricity the equations (1) give

$$\text{div.}\,X=-\tfrac{1}{3}\rho\frac{\partial\phi}{\partial x}+\tfrac{2}{3}\phi\frac{\partial\rho}{\partial x}=-\rho\frac{\partial\phi}{\partial x}+\tfrac{2}{3}\frac{\partial}{\partial x}(\rho\phi)$$

. . . .

There is thus an unbalanced body force $-\rho\nabla\phi+\frac{2}{3}\nabla(\rho\phi)$ which must be cancelled out by a body force exerted by the matter on the electricity. This new body force may be derived from the system of stresses (in the charged space)

$$X_x'=-\left(\frac{\partial\phi}{\partial x}\right)^2+\tfrac{1}{2}R^2-\tfrac{2}{3}\rho\phi+C,$$

$$X_y'=-\frac{\partial\phi}{\partial x}\frac{\partial\phi}{\partial y}=Y_x',$$

. . . .

where C is a suitable constant.

Adding the two distributions we obtain the stresses

$$X_x^*=-\tfrac{1}{4}\left(\frac{\partial\phi}{\partial x}\right)^2+\tfrac{1}{4}R^2-\tfrac{1}{4}\phi\frac{\partial^2\phi}{\partial x^2}-\tfrac{1}{4}\rho\phi+C-p,$$

$$X_y^*=-\tfrac{1}{4}\frac{\partial\phi}{\partial x}\frac{\partial\phi}{\partial y}-\tfrac{1}{4}\phi\frac{\partial^2\phi}{\partial x\partial y}=Y_x^*,$$

. . . .

and these should furnish the correct value for the stress between the body of a conductor and the outer layer containing the electric charge.

In the case of an electrified spherical soap-bubble we may write

$$\phi=f(r)$$

and consider the stress X_x^* at a point where $y=z=0$. Since

$$\frac{\partial^2\phi}{\partial x^2}=\frac{1}{r}f'+\frac{x^2}{r^2}f''-\frac{x^2}{r^3}f'$$

$$=f'' \text{ when } x=r,$$

we find that

$$X_x^*=\frac{1}{2r}ff'+C-p.$$

Now X_r^* should be continuous with the æthereal X_r at the outer spherical boundary $r=a$ and should consequently vanish

$$0=\frac{1}{2a}f(a)f'(a)+C-p,$$

$$X_r^*=\frac{1}{2r}.ff'-\frac{1}{2a}.f(a)f'(a).$$

At the inner spherical boundary of the electrified layer the electric field must vanish, consequently $f'(r)=0$, and so at this boundary the stress X_r^* is

$$X_r^*=-\frac{1}{2a}.f(a)f'(a).$$

Now $f(a)=\frac{e}{a}$, $f'(a)=-\frac{e}{a^2}$, where e is the total charge: hence the stress at this boundary has the usual value

$$X_r^*=\frac{e^2}{2a^4}.$$

It must be emphasized that the electrical layer is supposed to contain matter as well as electricity. An attempt to find a distribution of electricity in a spherical shell which will make the body force, $-\frac{1}{3}\rho\nabla\phi+\frac{2}{3}\phi\nabla\rho$, vanish and at the same time give no field at the internal boundary has proved unsuccessful.

§ 3. *The Parallel Plate Condenser.*

In a uniform electric field whose lines of force are parallel to Ox we may write

$$\phi=A+F.x,$$

where A and F are constants. At points in the æther we then have

$$X_x=\tfrac{1}{2}F^2,\quad Y_y=-\tfrac{1}{4}F^2,\quad Z_z=-\tfrac{1}{4}F^2,$$
$$Y_z=Z_x=X_y=0.$$

Inside the electrical layer we have simply (if $\phi=f(x)$)

$$X_x^*=C-p.$$

The stress component is thus constant and, being continuous with X_x at the boundary, must be equal to $\frac{1}{2}F^2$. This again agrees with the usual theory *.

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* It seems almost certain that we shall always obtain results agreeing with the usual theory if $\rho\phi$ is constant over each boundary of a layer of electricity.

It should be noticed that in this case we can find a volume distribution of electricity which will make the body force vanish, and so a layer consisting only of free electric charges seems to be theoretically possible.

The body force is zero, in fact, if

$$-\rho\frac{\partial\phi}{\partial x}+2\phi\frac{\partial\rho}{\partial x}=0,$$

i.e. if $\phi=b\rho^2$, where b is a constant. Since $\rho=-\frac{\partial^2\phi}{\partial x^2}$, we have the differential equation

$$\frac{\partial^2\phi}{\partial x^2}+\sqrt{\frac{\phi}{b}}=0$$

$$\therefore \qquad \left(\frac{\partial\phi}{\partial x}\right)^2=k^2-\tfrac{4}{3}\sqrt{\frac{\phi^3}{b}},$$

where k^2 is a new constant.

If ϕ and b are negative on the negative plate of the condenser we may suppose that $\frac{\partial\phi}{\partial x}=0$, $\phi=\phi_0$ for $x\leqq 0$, then

$$k^2=\tfrac{4}{3}\sqrt{\frac{\phi_0{}^3}{b}}.$$

The stress at $x=0$ given by equations (1) is now

$$X_x=-\tfrac{2}{3}\phi_0\frac{\partial^2\phi_0}{\partial x^2}-p=\tfrac{1}{2}k^2-p.$$

Since $\frac{\partial\phi}{\partial x}$ and the stress X_x should be continuous at the other boundary $x=a$ of the electrical layer

$$p+\tfrac{2}{3}\left(\phi\frac{\partial^2\phi}{\partial x^2}\right)_{x=a}=0,$$

i.e.

$$p=\tfrac{2}{3}\sqrt{\frac{\phi^3}{b}},$$

and the stress at $x=0$ is thus

$$X_x=\tfrac{1}{2}k^2-\tfrac{2}{3}\sqrt{\frac{\phi^3}{b}}=\tfrac{1}{2}\left(\frac{\partial\phi}{\partial x}\right)^2=\tfrac{1}{2}F^2,$$

which is the same value as before. The well-known formula for the stress can thus be obtained in a number of ways. The fact that it has been obtained in the new theory of electrostatics does not necessarily confirm this theory, for one is left with a suspicion that another theory based on a balance of forces may lead to the same result.

III. *The* CuH *Molecule and its Band Spectrum. By* HERBERT BELL, *Lecturer in Physics, University of Manchester* [*].

THE copper bands in the region λ 4700 to λ 4000 have recently been analysed by Frerichs in Bonn and Bengtsson in Lund [†], and the object of the present paper is to derive information from these regarding the copper atom.

Frerichs has represented the fine structure of the resolved bands by the formula

$$1/\lambda = A + B(m-\tfrac{1}{2}) + C(m-\tfrac{1}{2})^2 + D(m-\tfrac{1}{2})^3 + E(m-\tfrac{1}{2})^4, \quad (1)$$

and his table summarizing results is here reproduced.

n_1.	n_2.	Bands.	A.	B.	C.	D.	E.
0	0	4280	23318·16	13·497	−1·0702	−0·00190	0·000049
0	1	4650	21451·81	13·514	−0·8193	−0·00198	0·000052
1	0	4006	24929·07	12·973	−1·3395	−0·00206	0·000050
1	1	4328	23062·65	12·956	−1·0867	−0·00187	0·000053
1	2	4690	21270·50	12·993	−0·8304	−0·00221	0·000050
2	1	4063	24584·18	12·420	−1·3665	−0·00210	0·000021
2	2	4380	22792·57	12·418	−1·1228	−0·00214	0·000050

A striking feature is the constancy of the columns giving D and E. The parameter m has, as usual, integral values only and is zero for the "missing" or faint line of the band centre.

As is well known, these bands can be regarded as representing energy changes in the molecule caused by electric field and impact with neighbouring molecules. The molecule in a simple case may have m' quanta of angular momentum about an axis perpendicular to its axis of symmetry, where m' is not necessarily integral, together with n quanta of energy due to vibration along the axis of symmetry or line of join of nuclei. The differences in energy due to changes in m' and n give rise to what may be called "primary" bands situated for the most part in the infra-red, as in the case of the halogen hydrides discussed in a previous paper [‡].

If, now, there be superimposed upon this changes in the electron configuration within the molecule, then the energy changes will be much greater and "secondary" bands appear in the visible, as in the present instance. We shall take n' to represent the number of quanta possessed by the oscillating molecule in the higher configuration and n in the lower. Frerichs has assigned corresponding values n_1 and n_2 respectively for these states, as indicated in the first two columns of his table for the bands investigated. The correctness of his choice will be discussed below. He finds that the corresponding band centres ($m=0$) are well represented by the formula

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[*] Communicated by Prof. W. L. Bragg, F.R.S.

[†] Both articles appear in the same issue, Bd. xx. of the *Zt. für Physik*, and are in many respects identical.

[‡] Phil. Mag. xlvii. March 1924.

$$1/\lambda=23311{\cdot}15+1658{\cdot}81n_1-44{\cdot}71n_1^2-1903{\cdot}48n_2+37{\cdot}18n_2^2. \quad . \quad . \quad . \quad (2)$$

In discussing the halogen hydrides (*loc. cit.*) it was found convenient to use an expression derived by Born and Hückel for the energy W of an oscillating and rotating dumb-bell molecule, viz.:—

$$W^n_{m'}=U_0+nh\nu_0(1+\sigma m'^2)-n^2h\delta+\tfrac{1}{2}h\gamma m'^2-\tfrac{1}{2}h\gamma^3m'^4/\nu_0'^2. \quad . \quad . \quad (3)$$

U is the force function along the radius having values, along with its derivatives, at the position of equilibrium when at rest of U_0, U_0', U_0'', etc., r_0 is the distance between the nuclei when at rest, μ is the reduced mass, and ν_0 is the vibration frequency for small oscillations. The following abbreviations are here used:—

$$2\pi\nu_0=\sqrt{U_0''/\mu}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\beta=r_0U_0'''/U_0'', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\gamma=h/4\pi^2\mu r_0^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\delta=\frac{5\mu}{48}(\beta^2-3r_0^2U_0^{\text{iv}}/5U_0''), \quad . \quad . \quad . \quad (7)$$

$$\sigma=(\beta+2)\gamma^2/2\nu_0^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We shall assume that similar equations hold for both configurations of the present molecule, but in the higher configurations we shall replace U_0 ν_0 β γ δ σ by $U_0^{(1)}$ ν_0' β' γ' δ' σ' respectively. On changing from the higher configuration n' to the lower n the rotational quanta m' decrease algebraically by unity or from $m'+1$ to m'. The frequency of the emitted radiation is then given by

$$h\nu=W^{n'}_{m_1'+1}-W^n_{m'},$$

and on performing the necessary algebra we have

$$\nu=\underline{(U_0^{(1)}-U_0)}/h+\tfrac{1}{2}\gamma'+n'(\nu_0'+\nu_0'\sigma')-n'^2\delta'-n\nu_0+n^2\delta$$
$$+m'(\gamma'+2n'\nu_0'\sigma')+m'^2\{\tfrac{1}{2}(\gamma'-\gamma)-3\gamma'^3/\nu_0'^2+n'\nu_0'\sigma'-n\nu_0\sigma\}$$
$$-2m'^3\gamma'^3/\nu_0'^2-\tfrac{1}{2}m'^4(\gamma'^3/\nu_0'^2-\gamma^3/\nu_0^2). \quad . \quad . \quad . \quad (9)$$

[For the Q branch $\nu = (W^{n'}_{m'} - W^{n}_{m'})/h$

$$= (U_0^{(1)} - U_0)/h + n'\nu_0' - n\nu_0 - (n'^2\delta' - n^2\delta)$$

$$+ \tfrac{1}{2}m'^2\{\gamma' - \gamma + 2(n'\nu_0'\sigma' - n\nu_0\sigma)\} - \tfrac{1}{2}m'^4(\gamma'^3/\nu_0'^2 - \gamma^3, \nu_0^2).]$$

Determination of the Band Centre.

The parameter m' has not been assumed identical with m, and we shall write

$$m' = m - \epsilon, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where ϵ is a fraction, so that the angular momentum of the molecule is not zero at the centre unless $\epsilon = 0$ but changes from $(1-\epsilon)h/2\pi$ to $-\epsilon h/2\pi$. As (1) shows, Frerichs takes $\epsilon = \frac{1}{2}$ in agreement with Kratzer and other writers, and this value will be justified below.

It is noticed at once that (9) explains the fact, shown up in the table, that the coefficients of m^3 and m^4 are nearly constant from band to band. The value of ϵ does not affect this argument materially, since the successive coefficients B, C, D fall off so rapidly—B : C : D = 1 : 0·002 : 0·00005. Frerichs, not having the above formula, remarks that "the coefficients D and E, which are merely correction terms, show no systematic variation from band to band."

Heurlinger divides such bands as these into two series separated by the zero line, the P(m) series being to the left and the R(m) series to the right on a wave-number diagram. R(m) is identical with (9) for increasing values of m' from $m = 0$ onwards, while for P(m), $-m$ is written for m and the remaining lines are thus included. We can then break (9) up into

$$R(m) = \text{const.} + (m-\epsilon)(\gamma' + 2n'\nu_0'\sigma')$$

$$+ (m-\epsilon)^2(\text{const.} + n'\nu_0'\sigma' - n\nu_0\sigma) + \ldots$$

$$P(m) = \text{const.} + (-m-\epsilon)(\gamma' + 2n'\nu_0'\sigma')$$

$$+ (m+\epsilon)^2(\text{const.} + n'\nu_0'\sigma' - n\nu_0\sigma) + \ldots$$

where the constants do not involve m.

Subtracting, we have

$$R(m) - P(m)$$

$$= 2m(\gamma' + 2n'\nu_0'\sigma') - 4m\epsilon(\text{const.} + n'\nu_0'\sigma' - n\nu_0\sigma).$$

If $\epsilon = 0$ this function is independent of n, *i. e.* of the quantum number of the lower configuration or end stage. Similarly, if $\epsilon = -\frac{1}{2}$ the function is independent of n' the initial stage. Hence, if this function is formed for the various bands of the system and found to be identical for any set of them, we may deduce that these sets either have all the same initial stage and $\epsilon=0$, or all the same final stage and $\epsilon=-\frac{1}{2}$.

Similarly,

$$\begin{aligned}&R(m-1)-P(m+1)\\&\quad=2m(\gamma'+2n'\nu_0'\sigma')-4m(1+\epsilon)(\text{const.}+n'\nu_0'\sigma'-n\nu_0\sigma),\end{aligned}$$

which is independent of n if $\epsilon=-1$, and of n' if $\epsilon=0$. Both these difference functions $R(m)-P(m)$ and $R(m-1)-P(m+1)$ were applied by Frerichs to these bands and no identities found. On the other hand, he found that $R(m)-P(m+1)$ was identical for the three sets of bands λλ 4006, 4280; 4063, 4328, 4650; 4690, 4380. Similarly, $R(m)-P(m-1)$ was identical for the three sets λλ 4280, 4650; 4006, 4328, 4690; 4063, 4380.

Now,

$$\begin{aligned}&R(m)-P(m+1)\\&\quad=(2m+1)\{\gamma'+2n'\nu_0'\sigma'+(2\epsilon+1)(\text{const.}+n'\nu_0'\sigma'-n\nu_0\sigma)\}\end{aligned}$$

and

$$\begin{aligned}&R(m)-P(m-1)\\&\quad=(2m-1)\{\gamma'+2n'\nu_0'\sigma'+(2\epsilon-1)(\text{const.}+n'\nu_0'\sigma'-n\nu_0\sigma)\}.\end{aligned}$$

If $\epsilon=\frac{1}{2}$, the second difference is independent of n while the first one is independent of n'. *These bands can therefore be grouped into sets according to their initial and final configurations and at the same time the half quantum $\epsilon=\frac{1}{2}$ is justified.* This gives the grouping adopted by both Frerichs and Bengtsson as in the above table.

The band centres on substituting $m'=-\frac{1}{2}$ in (9) are now given by

$$\begin{aligned}\nu=(U_0^{(1)}-U_0)/h+\tfrac{1}{8}(\gamma'-\gamma)-\tfrac{1}{2}\gamma'^3/\nu_0'^2-\tfrac{1}{32}(\gamma'^3/\nu_0'^2-\gamma^3/\nu_0^2)\\+n'\nu_0'(1+\sigma'/4)-n'^2\delta'-n\nu_0(1+\sigma/4)+n^2\delta. \quad . \quad (11)\end{aligned}$$

Application of Formula.

Comparing equations (1) and (9) we have, since $m-\frac{1}{2}$ is now seen to be m',

$$cB=\gamma'+2n'\nu_0'\sigma', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$cC=\tfrac{1}{2}(\gamma'-\gamma)-3\gamma'^3/\nu_0'^2+n'\nu_0'\sigma'+n\nu_0\sigma, \quad . \quad (13)$$

and therefore

$$c(B-2C)=\gamma+6\gamma'^3/\nu_0'^2+2n\nu_0\sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

It follows that for series having the same end configuration (n' alone varying) cB should vary from band to band by the constant amount $2\nu_0'\sigma'$ and cC by the amount $\nu_0'\sigma'$. The following table shows how far this is fulfilled.

n_1.	n_2.	λ.	B.		C.	
0	0	4280	13·497		−1·0702	
				−·524		−·269
1	0	4006	12·973		−1·3395	
				...		
0	1	4650	13·514		−0·8193	
				−·558		−·267
1	1	4328	12·956		−1·0867	
				−·536		−·280
2	1	4063	12·420		−1·3665	
				...		
1	2	4690	12·993		−0·8304	
				−·578		−·292
2	2	4380	12·418		−1·1228	

Frerichs in fact derives from his table the relation

$$B=13{\cdot}50-0{\cdot}54n_1, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

more or less in agreement with this table, and therefore

$$2\nu_0'\sigma'=-0{\cdot}54c. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

Frerichs gives the further relation

$$C=-1{\cdot}07-0{\cdot}27n_1+0{\cdot}25n_2, \quad . \quad . \qquad (17)$$

from which, on comparing with (13),

$$\nu_0\sigma=-0{\cdot}25c. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

The Radial Quantum Numbers n', n.

We have now satisfied ourselves that the columns in Frerichs' table assigning integers to n_1, n_2 can be also assigned to n', n as regards the relative succession of values, but we have no means as yet of determining the absolute values of the latter. The values down the n column for example might all be increased by unity, as in fact Bengtsson has done for both columns. If we knew that the values of n_1, n_2 were also those of n', n respectively, we could equate coefficients in (2) and (11). Failing evidence, however, we write

$$n'=n_1+p', \qquad n=n_2+p,$$

and substitute in (2). Equating coefficients and using the known values of $\nu_0'\sigma'$ and $\nu_0\sigma$, we obtain

$$\delta'=44{\cdot}71c, \qquad \delta=37{\cdot}18c, \quad . \quad . \quad . \quad . \qquad (19)$$

$$\nu_0'/c=1658{\cdot}9+89{\cdot}4p', \quad . \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

$$\nu_0/c=1903{\cdot}5+74{\cdot}4p. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (21)$$

From (1) and (9) we have

$$D=\text{coefficient of } m'^3=-2\gamma'^3/c\nu_0'^2. \quad . \quad . \qquad (22)$$

Also
$$\gamma' - 0{\cdot}54n'c = c\mathrm{B} = (13{\cdot}50 - 0{\cdot}54n_1)c$$
by (15), so that
$$\gamma'/c = 13{\cdot}50 + 0{\cdot}54p'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$
Hence substituting in (22) from (20) and (23) we have, to a first approximation,
$$\mathrm{D} = -0{\cdot}00179(1 + 0{\cdot}012p'). \quad . \quad . \quad . \quad (24)$$
This gives Frerichs' values for D for the 4280 band for small values of p', but plainly D would need to be very exactly known to enable us to use (24) for determining p'. It does not seem possible therefore to determine p' and p from internal numerical relationships *.

By inspection, however, of (13) it is noticed that since $n'\nu_0'\sigma'$ and $n\nu_0\sigma$ are always small and C always negative,
$$\gamma' < \gamma, \ i.e. \text{ by (6) } r_0' > r_0.$$
Hence the nuclear separation decreases as the body falls back to the lower configuration. The force function, and its derivatives, is therefore very probably much diminished in the higher configuration and $\nu_0' < \nu_0$.

Now by inspection of (20) and (21) it is seen that, if p' exceeded p by more than 2, ν_0' would exceed ν_0, from which we deduce that $p' - p$ is in any case small. Both Frerichs and Bengtsson take $p' = p$ since this gives identical values for n' and n to the predominant band λ 4280. This assumption has since received justification from another quarter.

The Isotope Lines.

Frerichs finds for λ 4280 and λ 4328 that the lines of higher quantum number ($-m$) in the P series are accompanied by satellites on the short-wave side. These have since been attributed to the isotope Cu_{65} of copper by Mulliken †, who gives the formula for their distances from the main lines
$$\Delta\nu = (1 - \rho^2)s, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$
where s denotes the wave-number separation of the line from

---

* *The constant E.* From the values of γ and ν_0 given below we may similarly calculate the coefficient E,
$$\mathrm{E} = 0{\cdot}000078 - 0{\cdot}0000054p' + 0{\cdot}0000093p,$$
as against the value 0·000050 found by Frerichs. It must be kept in mind, however, that the coefficients of m'^4 are practically determined by quite a few lines at the end of the band and that, moreover, a more complete expansion might demand a term in m'^5 with consequent modification of E.

† 'Nature,' April 5th, 1924.

the band centre, and ρ is the ratio of the "respective molecular vibrations." By (4) $\rho^2=\mu_2/\mu_1$, where

$$1/\mu_2=1/M_2+1/m, \qquad 1/\mu_1=1/M_1+1/m,$$

and assuming, as established below, that $M\gg m$ we easily find that

$$1-\rho^2=m(M_1-M_2)/M^2.$$

The following table by Mulliken gives the agreement between observed and calculated values of $\Delta\nu$ for the two bands.

λ 4280 Band.

m.	*s.*	$\Delta\nu$ calc.	$\Delta\nu$ obs.
−22	804	0·39	0·31
−23	861	0·42	0·29
−24	920	0·45	0·45
−25	981	0·47	0·44
−26	1043	0·51	0·68
−27	1107	0·53	0·56
−28	1172	0·57	0·60

λ 4328 Band.

m.	*s.*	$\Delta\nu$ calc.	$\Delta\nu$ obs.
−17	539	0·32	0·23
−18	588	0·34	0·25
−19	639	0·37	0·26
−20	691	0·40	0·22
−21	746	0·42	0·45

The isotopes are all supposed to have the same arrangements of electrons, and since gravitational attraction plays only a negligible part in the dynamics of the system the quantities U_1, r and β in equations (4) .... (9) are unaffected. Other quantities are affected, through involving μ. We have

$$\Delta 1/\mu=1/\mu_2-1/\mu_1=(M_1-M_2)/M^2,$$

so that with $M\gg m$ as before,

$$\mu\Delta 1/\mu=1-\rho^2.$$

By (6), since $\gamma\propto 1/\mu$,

$$\Delta\gamma/\gamma=\mu\Delta 1/\mu=1-\rho^2.$$

Similarly, since by (4) $\nu_0\propto 1/\mu^{\frac{1}{2}}$,

$$\Delta\nu_0/\nu_0=\tfrac{1}{2}(1-\rho^2).$$

By (7) $\quad \Delta\delta/\delta=\Delta\gamma/\gamma=1-\rho^2,$

and by (4) and (8) $\quad \nu_0\sigma\propto 1/\mu_{3/2},$

so that $\quad \Delta\nu_0\sigma=\tfrac{3}{2}(1-\rho^2).$

Substituting these results in (9) we have

$$\begin{aligned}\Delta\nu/(1-\rho^2)&=(\nu_2-\nu_1)/(1-\rho^2)\\&=\tfrac{1}{2}(n'\nu_0'-n\nu_0)+3n'\nu_0'\sigma'(m'+\tfrac{1}{2})-(n'^2\delta'-n^2\delta)\\&\quad+(m'+\tfrac{1}{2})\gamma'+m'^2\{\tfrac{1}{2}(\gamma'-\gamma)-6\gamma'^3/\nu_0'^2+\tfrac{3}{2}(n'\nu_0'\sigma'-n\nu_0\sigma)\}\\&\quad-4m'^3\gamma'^3/\nu_0'^2. \quad . \quad (26)\end{aligned}$$

The distance *s* of the line from the band centre is obtained by subtracting (11) from (9). With the result thus obtained (26) can to a sufficient approximation be expressed in the form

$$(\nu_2-\nu_1)/(1-\rho^2)$$
$$=s+\tfrac{1}{2}(n'\nu_0'-n\nu_0)-(n'^2\delta'-n^2\delta)-2m'^3\gamma'^3/\nu_0'^2, \quad . \quad (27)$$

which is practically Mulliken's formula for $n'=n=0$. For the case of copper hydride $M_2-M_1=65-63=2$ and $m=1$, so that $1-\rho^2=-0{\cdot}00252$.

Taking $n'=n=1$ the correction to be applied to s by (27) amounts when multiplied by $1-\rho^2$ to $-0{\cdot}06$. With this correction the column $\Delta\nu$ calc. for $\lambda 4328$ is obtained. On the other hand, for $n'=n=0$ for $\lambda 4280$ (25) applies directly and the corresponding $\Delta\nu$ obtained. A further correction of 0·06 either way to these columns would be a definite misfit, and although the observed and calculated columns are not quite in step, we must conclude that $n'=n=0$ for $\lambda 4280$ and that therefore $p'=p=0$. A difference of unity or more in the n' n values for these bands would plainly, since ν_0 and ν_0' are large, be completely at variance with these results. Bengtsson takes $p'=p=1$ on account of two additional bands $\lambda 4607$ and $\lambda 4228$, which in the present scheme would require negative values of n' and n. The latter band, however, is obtained from earlier less accurate work of Hartley's, and the former, although visible on Bengtsson's plates, could not be analysed and may well belong to some other system.

Molecular Constants.

By (6),

$$r_0'^2=\frac{h}{4\pi^2\gamma'\mu}=\frac{h}{4\pi^2\gamma' M m_H}(1+M/X),$$

where M is the mass of the copper nucleus and X that of the other component of the molecule. Writing $M=63m_H$ and $X=xm_H$, where $m_H=1{\cdot}662\times10^{-24}$ gm. is the mass of the hydrogen nucleus, we obtain on substituting for γ' from (23), with $h=6{\cdot}55\times10^{-27}$ and $p'=0$,

$$r_0'=0{\cdot}1978\sqrt{1+63/x}\,.\,10^{-8}\text{ cm.}$$

Writing $x=1{\cdot}008$,

we have $r_0'=1{\cdot}578$ ångströms,

whereas $x=16$, corresponding to a CuO molecule or any similar heavy constituent, gives values of r_0' much smaller than is consistent with X-ray data for the radius of the copper atom. We are therefore dealing with a CuH molecule. The probability of this is kept in mind by Frerichs, who points out that the presence of hydrogen in some form is necessary for the production of the bands. Kratzer was the first * to point out that many of the metallic bands are due to hydrides.

From (14) and (18)

$$\gamma/c = \mathrm{B} - 2\mathrm{C} - 0{\cdot}006 = 15{\cdot}63,$$

and by (6) $$r_0 = 1{\cdot}467 \times 10^{-8}\,\mathrm{cm}.$$

Also $$r_0'/r_0 = \sqrt{\gamma/\gamma'} = 1{\cdot}076,$$

so that there is roughly an increase of 8 per cent. in linear dimensions in the higher configuration.

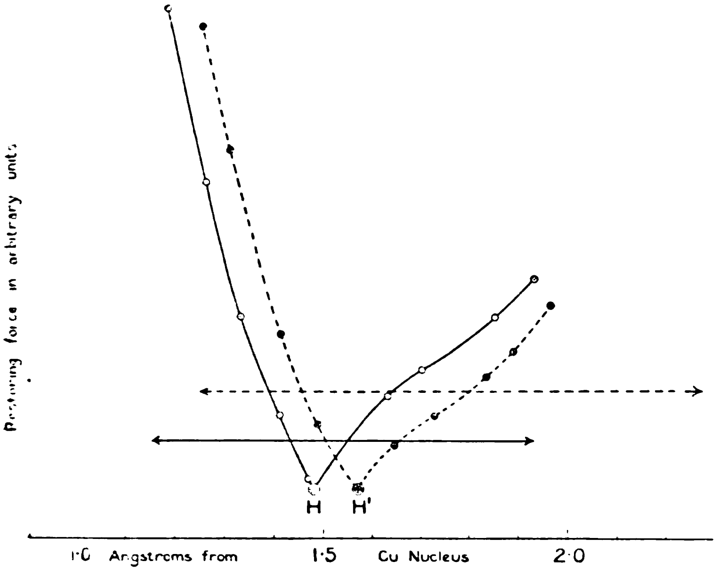
Again, $\nu_0'/c = 1658{\cdot}9$, $\nu_0/c = 1903{\cdot}5$.

These fundamental frequencies correspond to infra-red primary band systems of wave-lengths $6{\cdot}03\,\mu$ and $5{\cdot}25\,\mu$ respectively. If they or their overtones could be observed, the values of n' and n would be placed beyond doubt.

Solving equations (16), (18), and (8) we readily find

$$\sigma' = -1{\cdot}63 \times 10^{-4}\,; \qquad \sigma = -1{\cdot}32 \times 10^{-4},$$
$$\beta' = -7{\cdot}9 \qquad ; \qquad \beta = -6{\cdot}9.$$

Fig. 1.



The acceleration of the hydrogen nucleus when displaced a distance x from its equilibrium position is by formula (20) of the previous HCl paper given by

$$\ddot{x} = -4\pi^2\nu_0^2 x\{1 + \tfrac{1}{2}\beta\, x/r_0 + \tfrac{1}{18}(5\beta^2 - 48\,\delta/\gamma)(x/r_0)^2 + \dots\}.$$

This function is drawn to scale in arbitrary units in fig. 1.

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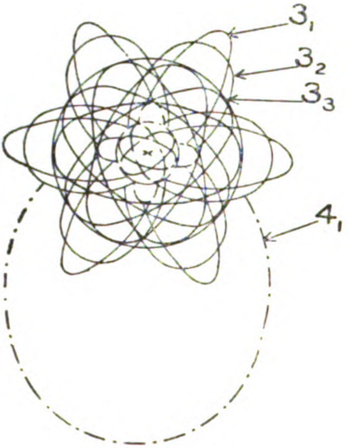
* *Ann. d. Phys.* lxxi. p. 102 (1923).

The full lines represent the lower configuration and the broken ones the higher. The greatest amplitude of oscillation in each case is also indicated by the horizontal lines. The acceleration curves are not drawn near the end of the oscillation range, since the above expansion is not convergent enough to be accurate for high values of x/r. The change from lower to higher configuration seems to be accompanied by a uniform expansion of the electric field.

Fig. 2 is a reproduction of the Kramers diagram for the copper atom.

Fig. 2.



The writer wishes to thank Professor W. L. Bragg for the facilities given and for his kindly interest in this work.

Summary.

A formula for band spectra in the visible is developed and applied to the copper bands recently measured by Frerichs and Bengtsson.

The half quantum for the rotating molecule is established and the molecule itself verified as being CuH.

The distances between the copper and hydrogen nuclei for the initial and final configurations are calculated and a diagram given showing the variation of the radial force function with distance.

Physics Department,
University of Manchester,
June 1924.

IV. *The Influence of the Length of the Radiating Column on the Width of Spectral Lines.* By B. VENKATESACHAR[*].

[Plate I.]

IN a paper entitled "On the Widening of Spectral Lines"[†] the late Lord Rayleigh has discussed the five possible causes of the widening of spectral lines.

The Doppler effect arising from the thermal agitation of the luminous centres (the first of the five causes) accounts, almost within the limits of experimental error, for the entire width of a line in the radiation from a thin layer of low-density luminous gas. In the case of a long column, "complications arising from the multiplicity of sources in the line of sight" must operate and increase the width of a line. The radiations corresponding to the less intense parts of a line in passing through the luminous vapour between the place of their origin and the observing optical system may be expected to suffer proportionately smaller absorption than the more intense radiations in the centre of the line, and therefore to be relatively brighter in the light from a long column than in that from a thin layer. A striking instance of the relative increase in brightness of the weaker members of a group of neighbouring lines in the radiation from a long column is provided by the line 5461 Å in the spectrum of the radiation from a low-density mercury-vapour lamp. When the light from a thin layer of the luminous vapour is examined in spectroscopes of high resolving power, this line can be resolved into a group of twelve lines of greatly varying intensity. But in the end-on radiation from a column one metre long carrying a current of not much more than 0·05 amp./sq. cm. all the satellites except $-0{\cdot}24$ are found to be nearly of the same brightness[‡]. Though an effect ot this kind ought to manifest itself in the case of a simple line, there seems to be no instance in which it has been detected or measured, for Lord Rayleigh in the paper alluded to says "it must certainly operate, and yet it does not appear to be important in practice." He alludes in his paper to some experiments carried out by him in which the radiation from a number of sodium flames placed one behind the other was examined. It was found that the presence of the flames behind the one nearest the observing system did not increase the brightness or the width of the D_1 and D_2 lines. Buisson and Fabry* in an important paper "on the width of spectral lines and the kinetic theory of gases" state that "this cause of widening can intervene in the case of flames of great thickness, but plays no role in the emission by the gas of Geissler tubes." In making reference to the case of flames of great thickness, these authors have possibly in mind Wanner's statement that he observed a broadening of the D lines in the radiation from a sodium flame placed between two concave mirrors. But Wood† has repeated these experiments, and does not confirm Wanner's observation. Hicks in his 'Analysis of Spectra' (1922, p. 14) says that "in practice, however, no effects are observed which can be put down to these causes," one of these causes being a possible damping of the emitted light, and the other the presence of a number of emitting centres in the line of sight. The heavy absorption exerted by luminous mercury vapour on the lines of the first and second subordinate series of triplets, viz. $1\,p_i-md$ and $1\,p_i-ms$, in the arc spectrum of mercury suggested to the author the possibility of detecting and measuring the widening due to this cause.

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[*] Communicated by Prof. A. W. Porter, D.Sc., F.R.S., F.Inst.P

[†] Phil. Mag. xxix. pp. 274-284 (1915).

[‡] Metcalfe & Venkatesachar, Proc. Roy. Soc. A, cv. pp. 520-531 (1924).

Preliminary Considerations.

(i.) In the case of a thin layer of low-density luminous gas the only cause of widening is the Doppler effect arising from the thermal agitation of the luminous centres. The distribution of intensity in such a case is governed by Maxwell's law of velocity distribution, and is represented by the relation

$$E=E_0e^{-k(\lambda-\lambda_0)^2}, \quad \ldots \ldots \quad (1)$$

where E_0 is the intensity of the line in the centre and E that at λ. Also

$$k=\frac{M}{2R\theta}\cdot\frac{c^2}{\lambda^2} \quad \ldots \ldots \ldots \quad (2)$$

and

M = mass of luminous centre,
R = the universal gas constant,
θ = the absolute temperature of the gas,
c = the velocity of light.

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* Buisson & Fabry, *Journ. de Phys.* ii. pp. 442–464 (1912).

† Wood's 'Optics,' p. 596.

If wave-length is replaced by wave-number $\nu=\frac{1}{\lambda}$, there will result for the distribution of intensity the relation

$$E=E_0e^{-k_1(\nu-\nu_0)^2},$$

where $$k_1=k\lambda^4.$$

(ii.) In an electrically excited gas it is not *a priori* certain that the temperature of the luminous part of the gas is the same as that of the containing tube. But the experimental work of Michelson, and subsequently of Buisson and Fabry, on the visibility of the interference fringes produced by electrically-excited luminous gases, clearly points to the conclusion that the temperature of the luminous part is not appreciably different from the temperature of the tube.

(iii.) The ratio of emission to absorption remains constant within a simple spectral line. In other words, if, in a simple line radiation from a thin layer of low-density luminous gas, E is the intensity of radiation at wave-length λ and A the corresponding coefficient of absorption, the ratio $\frac{E}{A}$ remains the same throughout the line. This constancy of $\frac{E}{A}$ throughout a simple spectral line may be shown to result from the following considerations based on the quantum theory. With Einstein, let us consider each individual act of emission or absorption of radiation by an atom as a directed process resulting in a transference of impulse to the atom. Let E_r and E_a represent the internal energies of an atom of the radiating gas in the emitting and absorbing states respectively. E_r and E_a are independent of the translatory motion of the atom. If an excited atom in the energy level E_r in passing to the energy level E_a emits in the line of sight the quantum $hc\nu$ of frequency $c\nu$, the resolved part of its velocity in this direction changes as a consequence of the recoil due to radiation from, say, u_1 to u_2. Considerations of energy and impulse before and after emission give respectively the equations:

$$\tfrac{1}{2}mu_1^2+E_r=\tfrac{1}{2}mu_2^2+E_a+hc\nu \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

and $$m(u_1-u_2)=\frac{hc\nu}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

As u_1 is small in comparison with c the velocity of light, higher powers of $\frac{u_1}{c}$ than the first do not matter, and the principles of ordinary mechanics are applicable. Writing $hc\nu_0$ for $E_r - E_a$, we get from (i.) and (ii.) the relation

$$\nu = \frac{\nu_0}{1 - \frac{u_1}{c} + \frac{u_1 - u_2}{2c}}.$$

Since $\frac{u_1 - u_2}{2c}$ is negligible in comparison with $\frac{u_1}{c}$, we may write

$$\nu = \frac{\nu_0}{1 - \frac{u_1}{c}} \text{ or } = \nu_0\left(1 + \frac{u_1}{c}\right); \quad . \quad . \quad . \quad \text{(iii.)}$$

and ν_0 may be taken to be the wave-number of the radiation emitted by an atom at rest. Equation (iii.) embodies the ordinary Doppler effect in the case of a source approaching the observer with velocity u_1.

Since an elementary act of absorption results in the transition of an atom from the energy level E_a to the energy level E_r, the quantum $hc\nu$ propagated in the line of sight may be absorbed by an atom in the state E_a, only when the line of sight component of its velocity just before absorption is u_2; for equations (i.) and (ii.) hold also in the case of absorption, and E_r, E_a, and ν remaining unaltered, u_1 and u_2 do not change. As has been pointed out before, $u_1 - u_2$ is negligible in comparison with u_1. In the case of an atom of mercury $u_1 - u_2$, i. e. $\frac{h\nu}{m}$, is about 0·36 cm. sec.$^{-1}$ for a line at 5461 Å. Therefore, in estimating the concentration of the emitters of any given frequency in a simple line radiation and that of the corresponding absorbers according to the Maxwellian law of distribution of velocities, we are justified in taking their respective velocities, viz. u_1 and u_2, to be equal.

In unit volume of a luminous gas the number of atoms dN in the energy level E_r, whose velocities in the line of sight lie between u and $u + du$, is given by

$$dN_r = N_r\sqrt{\frac{\beta}{\pi}}e^{-\beta u^2}du.$$

Similarly, the number of absorbing centres dN_a in the energy level E_a within the same range of velocities is

$$dN_a = N_a\sqrt{\frac{\beta}{\pi}}e^{-\beta u^2}du.$$

N_r and N_a are the respective concentrations of the atoms in the states E_r and E_a. If the frequency corresponding to the line-of-sight velocity u is $c\nu$, E the intensity of radiation at ν per unit thickness of a thin layer of unit cross-section is proportional to

$$N_r\sqrt{\frac{\beta}{\pi}}e^{-\beta u^2},$$

and the corresponding coefficient of absorption is proportional to

$$N_a\sqrt{\frac{\beta}{\pi}}e^{-\beta u^2}.$$

The ratio of emission to absorption at ν is given by

$$\frac{E}{A}=\frac{C_rN_r}{C_aN_a}, \quad \ldots \ldots \quad (\alpha)$$

and is the same at all points of the line. In (α), C_r may be termed the emission factor for the transition $E_r \rightarrow E_a$, and C_a the absorption factor for the transition $E_a \rightarrow E_r$. C_r has a significance analogous to that of the radioactive constant in radioactivity. C_r and C_a are independent of the mode of excitation of the gas, and depend only on the states E_r and E_a.

It is possible for two lines to have the same ratio $\frac{N_r}{N_a}$, and yet for $\frac{E}{A}$ to vary from one line to the other on account of the factors C_r and C_a being different for the two. In the case of elements of group II. of the periodic table, emission and absorption lines corresponding to $1\,S-1p_1$ and $1\,S-1p_3$ have not been detected, and are ruled out according to Sommerfeld by the principle of selection. In these cases C_r and C_a separately vanish. For corresponding lines of isotopes we should expect the ratio of emission to absorption to be the same, for the factors C_r and C_a and the concentration ratio of the emission and absorption centres, viz. $\frac{N_r}{N_a}$, of one line are the same as the corresponding ones of the other.

$\frac{N_r}{N_a}$ may depend on the mode of excitation of the gas. It was found by Metcalfe and the author* that low-density mercury vapour through which a true arc discharge is passing exhibits much higher absorption for lines of the series $1p_i-md$ and $1p_i-ms$ than when the discharge is not a true arc discharge, though the emission line may be actually brighter in the latter case.

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* Proc. Roy. Soc. A, c. pp. 149–166 (1921).

To take a particular instance, in a mercury-vapour lamp designed so as to run on low current densities, in which the length of the discharge was 13 cm., there was a sudden and marked increase in the absorption exhibited by the luminous vapour for lines of the series mentioned above, when the voltage between the electrodes fell from 60 to 20 volts. Since the emitting centres are in higher energy levels than the corresponding absorbing centres, the above experimental result implies that the conditions in an arc discharge are favourable for the production of excited atoms of lower energy level in relatively larger numbers than in a non-arc discharge. For pressures of the order of 0·1 mm. of mercury the electric intensity in luminous mercury vapour is least, and is approximately independent of the current density when the radiation is the result of an arc discharge. It appears, therefore, that an increase in the electric intensity has the effect of producing a relatively larger number of excited atoms in higher energy levels. It is of interest to remember in this connexion that a rise of temperature in thermal excitation increases in concentration of atoms in higher energy levels.

I.

Intensity distribution in a simple line radiated from the end of a luminous column of finite length.

Let AB represent a column of luminous gas contained in a uniform tube of unit cross-section, the observer's spectroscope being situated on its axis at a distance large compared with the length of the column. If $E_0 dx$ is the intensity in the middle of the line radiated by a thickness dx along the axis of the tube, the intensity at wave-length λ is given by

$$E dx = E_0 e^{-k(\lambda-\lambda_0)^2} dx.$$

Representing the coefficient of absorption per unit thickness of the column for radiation of wave-length λ by A, we write $A dx$ for the coefficient of absorption of a layer of thickness dx.

The ratio

$$\frac{E dx}{A dx} = \frac{E_0 e^{-k(\lambda-\lambda_0)^2}}{A}$$

is the same at all points of the line, and will be denoted by I and

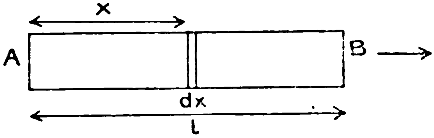
$$A = \frac{E_0}{I} e^{-k(\lambda-\lambda_0)^2} = A_0 e^{-k(\lambda-\lambda_0)^2},$$

where A_0 is the coefficient of absorption for radiation of wave-length λ_0 corresponding to the centre of the line.

The axial radiation dR along AB in the wave-length interval λ and $\lambda+d\lambda$ from an element dx at a distance x from the remote end A of the radiating column AB of length l is given by

$$dR = Ee^{-A(l-x)}dx\,d\lambda.$$

Fig. 1.



So the radiation along AB from the whole column l is given by

$$\int dR = Ed\lambda \int_0^l e^{-A(l-x)}dx$$

$$= \frac{Ed\lambda}{A}\left(1-e^{-Al}\right)$$

$$= Kd\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Making the substitutions I and $A_0 e^{-k(\lambda-\lambda_0)^2}$ for $\frac{E}{A}$ and A respectively in (3), we get for the intensity distribution in the line radiated by the column the equation

$$K = I\left\{1-e^{-A_0 l e^{-k(\lambda-\lambda_0)^2}}\right\}. \quad . \quad . \quad . \quad . \quad (4)$$

Writing K_0 for the intensity in the centre of the line, *i. e.* at $\lambda-\lambda_0=0$,

$$\frac{K}{K_0} = \frac{1-e^{-A_0 l e^{-k(\lambda-\lambda_0)^2}}}{1-e^{-A_0 l}} = r\ (\text{say}), \quad . \quad (5)$$

which leads to the relation

$$\lambda-\lambda_0 = \left\{\frac{\log F}{k}\right\}^{\frac{1}{2}},$$

where
$$F = \frac{A_0 l}{\log D}$$

and
$$D = \left\{1-r+re^{-A_0 l}\right\}^{-1}. \quad . \quad . \quad . \quad . \quad (6)$$

In order to draw the intensity curve, the values of $\lambda-\lambda_0$ are calculated for assigned values of r, i. e. $\frac{K}{K_0}$. In the following calculations I have taken the case of a luminous column one metre long. This length was actually used in certain absorption experiments by Metcalfe and the author (*loc. cit.*). 0·4 is taken as the value of A_0. This was the experimental value of the absorption coefficient for the complete green-line group 5461 Å in the radiation of low-density mercury vapour carrying a current of 20 milliamperes per sq. cm., so that 0·4, the coefficient in the centre of a simple line, say the main line of 5461 Å group under the conditions of the experiment alluded to, is, if anything, an underestimate.

In the following table the ratios (r) of the intensities at different points in the line to that at the centre are shown against the positions $\lambda-\lambda_0$, the temperature being 400° absolute.

TABLE I.

$r=\frac{K}{K_0}$.	$\lambda-\lambda_0$.
·99	·00488
·90	·00560
·80	·00595
·70	·00621
·50	·00668
·30	·00721
·20	·00756
·10	·00808
·05	·00855

The results are shown graphically in fig. 2.

For purposes of comparison, the intensity distribution curve for the radiation from a thin layer is also shown. The wave-length scale is the same for both curves, but the intensity scale in the case of the thin-layer radiation is so chosen as to make the curves touch at $\lambda=\lambda_0$.

If with Rayleigh we denote the half-width of a symmetrical line as the wave-length separation * between its centre and a point on either side where the intensity falls to one-half the maximum and denote it by w, we see that the half-width of the line radiated by a column of vapour one metre long considered above is more than twice that of the same line radiated by a thin layer under the same conditions of experiment, the calculated half-width in the latter case being 0·0027 Å.

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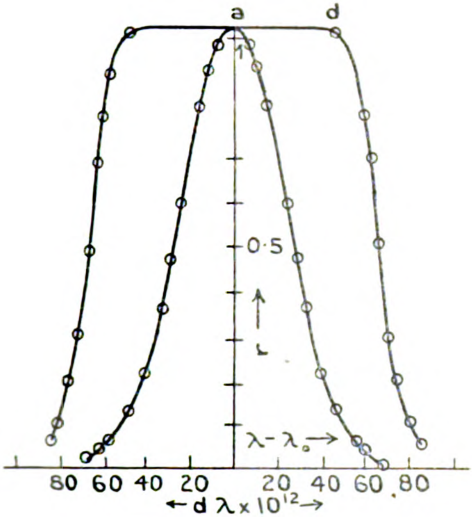
* There is some diversity in the conventional definition of the width of a line. According to the above definition the width is $2w$. Buisson and Fabry substitute $2·3w$ for $2w$. According to others, the width of a line is the wave-length separation between two points where the intensity is $\frac{1}{e}$th of the maximum, about $2·4w$.

The marked flattening of the curve in the middle of the line has a large influence in reducing the resolvability of two neighbouring lines. Two lines having the same coefficient of absorption, $A_0=0{\cdot}4$, and separated from each other by a wave-length distance of 0·01 Å $=2ad$ (see fig. 2), could be separated in a spectroscope of the necessary resolving power (of the order of 700,000) when the source is a thin layer of the luminous vapour; on the other hand, the lines would coalesce and not be separated in the axial radiation of the long column considered, however high the resolving power of the spectroscope may be. Of the satellites of the complex mercury line 5461 Å, the two closest to the main line are of wave-lengths +·0086 Å and −·0087 Å. Since the half-width of the main line is about ·0027 Å, a spectroscope whose resolving power is about 700,000 would show the side satellites separate from the main line in the radiation from a thin layer; whereas, if the radiation is from a long column of the vapour under suitable conditions of excitation, the widened satellites would fuse with the main line, and not be separated

Fig. 2.



from it in any spectroscope. Further reference will be made to this aspect of the question in describing experiments in which the widening of lines has been observed.

II.

The evaluation of the energy content of a line radiated from the end of a column of finite length.

The radiation in the wave-length range λ and $\lambda + d\lambda$ is given by

$$K d\lambda = I\left\{1 - e^{-A_0 l e^{-k(\lambda-\lambda_0)^2}}\right\} d\lambda. \quad . \quad . \quad (7)$$

The energy content of the line on expanding the exponential becomes

$$\int K d\lambda$$

$$= I \int_{\lambda-\lambda_0=-\infty}^{\lambda-\lambda_0=\infty} \left\{ A_0 l\, e^{-k(\lambda-\lambda_0)^2} - \frac{(A_0 l)^2}{2\,!} e^{-2k(\lambda-\lambda_0)^2} + \dots \text{ad inf.} \right\} d\lambda.$$

Finally, writing ξ for $A_0 l$, we have

$$\int K d\lambda$$

$$= I\sqrt{\frac{\pi}{k}}\left\{\xi - \frac{\xi^2}{2\,!\,\sqrt{2}} + \frac{\xi^3}{3\,!\,\sqrt{3}} - \dots \text{ad inf.}\right\}. \quad . \quad . \quad (8)$$

The summation of the series inside the brackets (S), correct to three places of decimals for values of ξ even as low as 4 or 5 requires the use of an inconveniently large number of terms. When ξ is more than 10, the summation becomes hopelessly cumbersome. In Table II. the calculated values of S are shown against the corresponding values of ξ.

TABLE II.

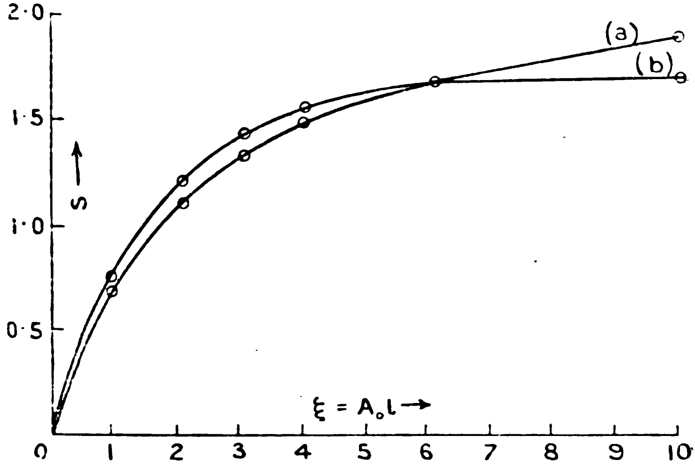
ξ.	S.
1	·725
2	1·112
3	1·341
4	1·489
5	1·593
6	1·672
10	1·909

The dominant term in the asymptotic expansion of the above series S has been determined by G. H. Hardy *, and is

$$2\left\{\frac{\log \xi}{\pi}\right\}^{\frac{1}{2}}$$

This term alone will give the value of S for very large values of ξ. The accompanying diagram (fig. 3, a) represents the relation between $A_0 l$ and the radiation along the axis (fig. 3). It is plain that the radiation from a luminous column does not asymptotically approach a finite value as the length of the column is increased. Nevertheless, it is manifest that

Fig. 3.



for large values of ξ—i. e. $A_0 l$—the rate of increase of S with ξ is small, and approaches zero as ξ approaches infinity; for instance, if we have a luminous column of mercury vapour one metre long, and the current density is so adjusted that the absorption coefficient is ·05, $A_0 l = 5$ and $S = 1·593$ (see Table II.). If the column is doubled, other conditions remaining the same, $A_0 l = 10$ and $S = 1·909$. Therefore doubling the column does not alter the radiation by more than 0·316, *i. e.* by more than about 20 per cent. If the coefficient of absorption is considered to remain constant throughout the line and equal to 0·56 A_0, which is its mean value between the centre of the line and a point where the intensity is 1/10 that at the centre, the radiation R from a column of length l is given by

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* Proc. of the London Math. Soc. ser. 2, ii. p. 428 (1904).

$$R = 1{\cdot}78\, I\left(1 - e^{-0{\cdot}56\, A_0 l}\right)\sqrt{\frac{\pi}{k}}.$$

The radiation asymptotically approaches the value $1{\cdot}78\, I\sqrt{\frac{\pi}{k}}$.

In the case of two neighbouring lines which have the same ratio of emission to absorption but are of unequal intensity in the radiation from a thin layer, the weaker one approaches in brightness the stronger line on increasing the length of the radiating column. If the absorption coefficient is not taken to vary from point to point of a line, the weaker line should more rapidly approach in brightness the brighter one as the length of the radiating column is increased than if the coefficient varied from point to point as postulated in the above discussion. Certain experiments carried out by Metcalfe and the author on the components of the green-line group 5461 Å in the radiation from long columns distinctly support the latter postulate (*loc. cit.*).

Experimental evidence of the widening of lines due to length of radiating column.

As the width of a simple line of the 5461 Å group in the axial radiation from a long column of low-density mercury vapour, through which an arc discharge is passing, is of the order of ·014 Å at a temperature of 400° absolute, the corresponding width in the case of the thin-layer radiation being ·006 Å, it becomes necessary to use instruments of high resolving power in experiments carried out with the object of observing the change of width from ·006 Å to ·014 Å when the illuminating source is changed from a thin layer to a long column. In the experiments described below a Lummer-Gehrcke plate, made by Hilger and of resolving power exceeding 200,000 at 5461 Å, was used in conjunction with a constant deviation spectroscope which produced the preliminary dispersion. For a proper understanding of the experiments described below, proving the existence of the widening of lines we have been considering, a knowledge of the performance of the resolving apparatus used is essential. The following are the data of the Lummer and Gehrcke plate I have used in these experiments:—

d (plate thickness) $= 0{\cdot}47$ cm.,

μ at 5461 Å $= 1{\cdot}51108$,

$$\frac{d\mu}{d\lambda} = -509,$$

$$\delta\lambda = {\cdot}2712 \text{ Å}.$$

The relative positions of the components of the 5461 Å group between two successive orders of the main line are shown in fig. 4, where the full lines stand for the *n*th order components and the dotted ones for those of the *n*+1th order.

The mercury-vapour lamp shown in fig. 5 (i.), was constructed with the object of providing a long low-pressure radiating column GH (length 30 cm. and diameter of tube 0·8 cm.). The horizontal part is the seat of the long column

Fig. 4.

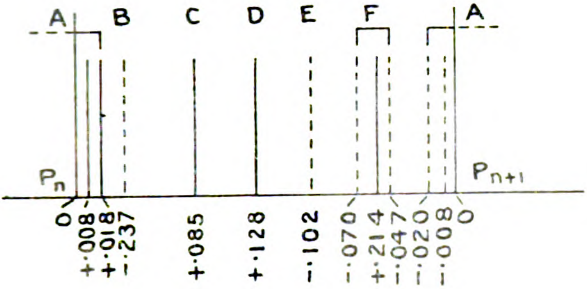
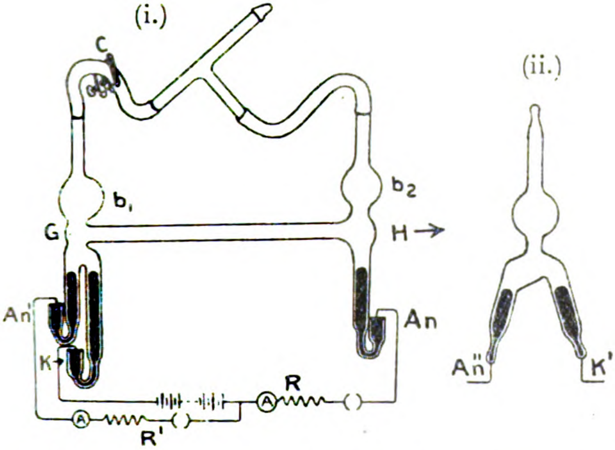


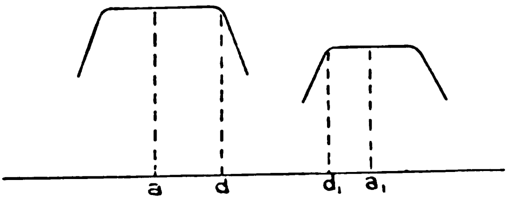
Fig. 5.



arc discharge between the electrodes An and K. In order to facilitate the starting of this arc, provision is made to run a subsidiary arc between electrodes An′ and K, K functioning as the common cathode for the two arcs. The tube is provided with two bulbs, b_1 and b_2, which are intended to condense the vapour issuing from the anodes and the common cathode when the lamp is running. The lamp is evacuated by a mercury pump till the pressure falls below ·01 mm. of mercury. The passage above the subsidiary arc leading to the pump is closed by the screw clip C and the subsidiary arc started. As soon as the stream of mercury vapour issuing from this arc reaches the surface of the anode An, the long arc GH starts, and the resistance R is adjusted so that the current in GH is not less than 1·5 amp. The subsidiary arc is now quenched without affecting the steady running of the main arc. In order to prevent the rush of mercury vapour along GH, connexion with the pump along GC is restored by loosening the clip C. The observing apparatus, consisting of a constant deviation spectroscope and the Lummer-Gehrcke plate already referred to, is placed properly aligned at sufficient distance from the tube to ensure full effectiveness from all parts of the arc GH. When the green-line group 5461 Å is examined in this apparatus, with the resolving plate in position, the difference between the pattern produced by the radiation from the arc just above the anode (thin layer) and that due to the long column radiation is very striking. In addition to being greatly enhanced, all the lines except −·24 are distinctly widened, with the result that the lines of demarcation between the several components become so indistinct that the pattern may be easily mistaken for one produced by a high-pressure lamp. In the reproduction (Pl. I. fig. I) the enlarged pictures of the two patterns are shown in juxtaposition. The appearance presented by −0·24 and +·085, marked B and C, is particularly interesting. In the thin-layer pattern I (*a*), −0·24 is hardly visible, whereas +·085 is bright and sharp, but in pattern I (*b*), produced by the long column, B, −0·24 is greatly enhanced in brightness owing to feeble absorption, and stands out as the brightest and sharpest line of the group, whereas C, +·085, the heavily-absorbed satellite, is comparatively weak but distinctly widened. The difference in sharpness, striking as it is in the reproduction, is much more so when observed in the instrument. The most convincing proof of widening is no doubt to be looked for in the disappearance of the line of demarcation between two close lines as the illuminant is changed from the thin layer to the long column. In fig. 4 are shown the relative positions of the lines in the observed pattern; at P_{n+1} the main line O and the close lines −·008 and −·020 are not resolved in the instrument. The line of separation between groups A and F was very distinct in the thin-layer pattern, but was entirely absent in the pattern due to the long column when the current in it was of the order of 1·5 amp. This is distinctly shown in the reproduction (see Pl. I. fig. I). Here again the actual appearance in the instrument is much more pronounced and striking. In this case ξ the product of the coefficient of absorption and the length of the radiating column is of the order of 1000 for $-0·020$ Å.

The wave-length separation $a\,d$ (see fig. 2) between the centre of the line and the point on one side where the intensity falls to (say) 0·99 of that at the centre increases with $A_0 l$ (see fig. 6). Therefore $a\,d$ for the line $-0·020$ Å, which is more heavily absorbed, is greater than $a\,d$ for the line $-·047$ Å. If from ·027 the wave-length distance between the lines $-·047$ Å and $-·020$ Å we subtract $a\,d + a_1\,d_1$ (see fig. 6), which is approximately ·014, we get ·013, and if the instrument is unable to resolve two lines with a separation of ·013 Å, the line of demarcation disappears: and this is so in the case of the instrument used.

Fig. 6.



In this method of observation the instrumental width of a line and its physical width are made to assist each other in wiping out the line of separation between two close lines.

If, however, $a\,d + a_1\,d_1 \geq aa_1$, the two lines fuse together and the line of demarcation disappears, even in an instrument of infinite resolving power, for which the instrumental width of a line is zero. The observed effect is not due to the brightening-up of the group F in a long column. In order to make sure on this point, an experiment was made using as source an arc produced in the tube shown in fig. 5, ii. The pressure was increased to 1 cm. of mercury by the introduction of air, and the arc was run with a current of 2 amp. The group of lines F increased very much in brightness, and the line of demarcation between F and A was distinctly visible. Neither the increase of width due to a pressure of 1 cm. nor the consequent increase of brightness could blur the line of separation; if anything, the line of separation was more distinct than before the increase of pressure and current. With an *echelon* spectroscope of resolving power 100,000, the line of demarcation between +·085 and +·128, sharp in the pattern produced by the radiation from a thin layer, was distinctly blurred in that of the long-column radiation. The resolving power was reduced by diminishing the aperture of the *echelon* till the line of demarcation between these satellites disappeared in the long-column pattern. Under these conditions the use of a thin luminous layer in place of the long column again revealed the separating line.

The group of lines 5769 Å and 5790 Å were similarly examined, and it was found that the satellites +·044 Å and −·050 Å for 5769 Å were distinctly widened in the long-column radiation, with the result that the lines separating them from the main line, which are sharp in the Lummer-plate pattern, due to the thin-layer radiation, grew indistinct when the long column, GH, was used as the source. These satellites and the main line have been reversed on a continuous background by Metcalfe and the author (*loc. cit.*).

In the case of 5790, the satellites are very much brighter in the long-column radiation, but remain sharp and well separated from each other. This result is in agreement with the fact that it was not possible to reverse them on a continuous background, indicating that their absorption coefficient is of a different order from that of the two satellites of 5769 Å.

Experiments proving the existence of the widening indicated by the theory having been described, the rest of the paper is devoted to a discussion of the bearing of this widening on certain physical investigations in which experimental methods depending on the visibility of interference fringes have been employed. As preliminary to the discussion, the following problem is considered.

III.

The visibility of interference fringes produced by the axial radiation from a luminous column of finite length in an interferometer of the Michelson type.

In the case of a thin layer of gas at a low pressure, in which the emitting centres have a velocity distribution governed by Maxwell's law, the visibility of the interference fringes in an interferometer which produces the pattern by splitting the incident beam into two of equal intensity and after they have travelled different distances subsequently combining them, has been worked out by the late Lord Rayleigh, and is given by

$$V = e^{\frac{-2\pi^2 R}{c^2}\left(\frac{2p}{\lambda}\right)^2 \frac{\theta}{M}}, \quad . \quad . \quad . \quad . \quad (9)$$

where the visibility V, according to Michelson,

$$= \frac{\text{I max.} - \text{I min.}}{\text{I max.} + \text{I min.}} \qquad \text{I} = \text{intensity},$$

and $2p$ = the path-difference between the interfering beams.

As a result of photometric experiments, Lord Rayleigh (*loc. cit.*) arrived at the result that the variation of brightness from a maximum to a minimum cannot be recognized when V falls to $\frac{1}{40}$, *i.e.* to ·025.

Setting $\frac{1}{40}$ for V in (9), we get for $\frac{2p}{\lambda}$

$$\frac{2p}{\lambda} = N_0 = \frac{c}{\pi}\sqrt{\frac{\log 40}{2R}}\sqrt{\frac{M}{\theta}}$$

$$= 1{\cdot}427\sqrt{\frac{M}{\theta}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The expression for the visibility takes a more complicated form in the case of a column of finite length. If two coherent beams of equal intensity and wave-number ν overlap, they produce an illumination which is given by

$$2A^2(1 + \cos 4\pi p\nu),$$

where A^2 is the intensity of either beam and $2p$ is their path-difference. If the source which has given rise to the two interfering pencils gives a line with an intensity distribution given by (say) $\psi(x)$, where x is the wave-number distance from the centre of the line, the illumination at the point of the interference pattern under consideration is to be evaluated by summing up the illuminations due to the several elements into which the radiation line may be split up. The illumination dI due to the radiations in the wave-number range x and $x + dx$ is given by

$$dI = \psi(x)\{1 + \cos 4\pi p(\nu_0 + x)\}dx, \quad . \quad . \quad (11)$$

where ν_0 is the wave-number for the centre of the symmetrical line. The illumination at the point is obtained by integrating

(11) between the limits $+\infty$ and $-\infty$.

$$\int dI = \int_{-\infty}^{+\infty} \psi(x)\{1 + \cos 4\pi p(\nu_0 + x)\} dx$$

$$= \int_{-\infty}^{\infty} \psi(x) dx + \cos 4\pi p\nu_0 \int_{-\infty}^{\infty} \psi(x) \cos 4\pi px\, dx$$

$$- \sin 4\pi p\nu_0 \int_{-\infty}^{\infty} \psi(x) \sin 4\pi px\, dx,$$

and $\psi(x)$ by a slight transformation of (6) is given by

$$K d\nu = \psi(x) dx$$

$$= I\left\{1 - e^{-\xi e^{-k_1 x^2}}\right\} dx.$$

As the line is symmetrical, the third integral is zero. Let the first and the second integrals be represented by C and D respectively.

$$C = \int_{-\infty}^{+\infty} \psi(x) dx$$

$$= I\sqrt{\frac{\pi}{k_1}} \left\{\xi - \frac{\xi^2}{2!\sqrt{2}} + \frac{\xi^3}{3!\sqrt{3}} - \frac{\xi^4}{4!\sqrt{4}} + \dots\right\} \quad (12)$$

The second integral may be written thus

$$D = I \int_{-\infty}^{+\infty} \left[\xi e^{-k_1 x^2} - \frac{\xi^2}{2!} e^{-2k_1 x^2} + \frac{\xi^3}{3!} e^{-3k_1 x^2} - \dots\right] \cos 4\pi px\, dx.$$

Hence we have

$$D = I\sqrt{\frac{\pi}{k_1}} \left\{\xi e^{-\frac{4\pi^2 p^2}{k_1}} - \frac{\xi^2}{2!\sqrt{2}} e^{-\frac{4\pi^2 p^2}{2k_1}} + \dots\right\} \quad . \; . \quad (13)$$

The intensity I is given by

$$I = C + D \cos 4\pi p\nu_0.$$

Since the brightness of a line is reduced almost to zero at a wave-number distance x from the centre which is very small compared with ν_0, the variation of intensity in any given region of the interference pattern is governed by $\cos 4\pi p\nu_0$;

i. e. a variation in $2p$ which changes the value of $\cos 4\pi p\nu_0$ from $+1$ to -1 does not produce any appreciable difference in D. Therefore $I_{\text{max.}} = C + D$ and $I_{\text{min.}} = C - D$;

i. e.,
$$V = \frac{I_{\text{max.}} - I_{\text{min.}}}{I_{\text{max.}} + I_{\text{min.}}}$$

$$= \frac{D}{C}$$

$$= \frac{\xi e^{-\frac{4\pi^2p^2}{k_1}} - \frac{\xi^2}{2!\sqrt{2}} e^{-\frac{4\pi^2p^2}{2k_1}} + \frac{\xi^3}{3!\sqrt{3}} e^{-\frac{4\pi^2p^2}{3k_1}} - \dots}{\xi - \frac{\xi^2}{2!\sqrt{2}} + \frac{\xi^2}{3!\sqrt{3}} - \dots} \qquad \dots\dots\dots \quad (14)$$

As the path-difference $2p$ increases, the clearness of the fringes falls, and when $2p$ assumes the value which makes $V = 0{\cdot}025$, they become unrecognizable;

i. e.,
$$\frac{\sum_1^\infty (-1)^{n-1} \frac{\xi^n}{n!\sqrt{n}} (\chi)^{\frac{1}{n}}}{\sum_1^\infty (-1)^{n-1} \frac{\xi^n}{n!\sqrt{n}}} = 0{\cdot}025, \quad \dots \quad (15)$$

where
$$\chi = e^{-\frac{4\pi^2p^2}{k_1}}.$$

It is easily seen that (15) reduces to $e^{-\frac{4\pi^2p^2}{k_1}} = 0{\cdot}025$ when A_0l approaches zero, *i. e.* to Rayleigh's equation (10) for the case in which there is no absorption or the radiating layer is thin.

For assigned values of ξ (*i. e.*, A_0l,) χ may be evaluated by a somewhat laborious method of successive approximation.

TABLE III.

$\xi = A_0l$.	χ.
0	·025
1	·091
2	·165
3	·233
4	·295
5	·350
10	·565

For large values of ξ the method becomes too cumbersome. In this case, however, the visibility can be calculated by considering the graph of the intensity distribution curve to be a trapezium with a flat top (see fig. 2). In the case $A_0 l=40$ this method has been adopted. The result so obtained is sufficiently accurate for all practical purposes.

Now, since $\chi=e^{-\frac{4\pi^2 p^2}{k_1}}$, we get by suitable transformation after making the substitution $k_1=k\lambda^4=\frac{M}{2R\theta}c^2\lambda^2$,

$$N=\frac{2p}{\lambda}=\frac{c}{\pi}\left\{\frac{-\log\chi}{2R}\right\}^{\frac{1}{2}}\sqrt{\frac{M}{\theta}}$$

$$=\phi(A_0 l)\sqrt{\frac{M}{\theta}}\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

For a thin layer we have from (10):

$$N_0=\frac{2p_0}{\lambda}=\frac{c}{\pi}\left\{\frac{\log 40}{2R}\right\}^{\frac{1}{2}}\sqrt{\frac{M}{\theta}}\,.$$

Therefore

$$\frac{N}{N_0}=\left\{\frac{-\log\chi}{\log 40}\right\}^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

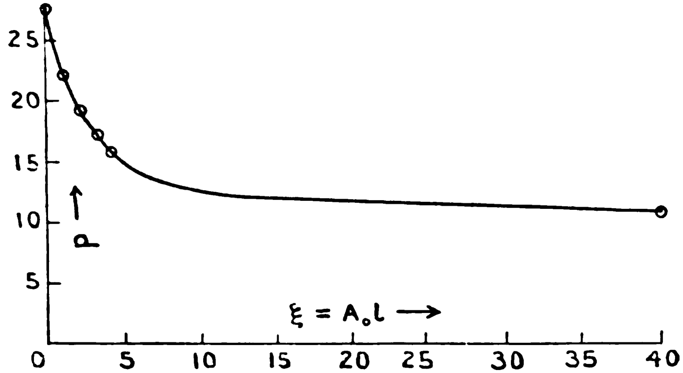
Buisson and Fabry have replaced 1·427 by 1·22 in (10). This means that according to these authors the fringes cease to be recognizable for values of V higher than ·025. In the calculations embodied in this paper, Lord Rayleigh's value 0·025, based on photometric measurements carried out by him, has been used. The use of 0·025 gives higher values for the limiting order of interference at which the fringes cease to be visible, and hence supplies a more severe test of the widening of lines.

TABLE IV.

ξ.	χ.	$\frac{N}{N_0}$.	N.	p.
0	·025	1·000	$1·01 \times 10^6$	27·5 cm.
1	·091	·805	$·81 \times 10^6$	22·1 ,,
2	·165	·699	$·70 \times 10^6$	19·2 ,,
3	·233	·628	$·63 \times 10^6$	17·3 ,,
4	·295	·573	$·578 \times 10^6$	15·8 ,,
5	·350	·531	$·537 \times 10^6$	14·7 ,,
40	·565	·396	$·40 \times 10^6$	10·9 ,,

According to this, the difference of path $2p$ when the fringes become unrecognizable should fall from $2 \times 27{\cdot}5$ cm. to $2 \times 17{\cdot}3$ cm. when the thickness of the radiating column is increased from 0 to 7 cm. in the case of the arc discharge of mercury vapour considered for which the coefficient of absorption is 0·4 per cm.; when the thickness of the layer is increased to one metre, it should fall to 2×11 cm., *i. e.* to 40 per cent. of the value for a thin layer. If a Fabry and Perot interferometer be used, and if the above result which has been obtained by considering only two coherent rays of equal intensity be taken to be applicable to this case also, the fringes should become invisible when the distance between the plates is 11 cm., but with a thin luminous layer under the same conditions of excitation as source they should be recognizable even when the distance is as much as 27·5 cm.

Fig. 7.



The experimental verification of this result in the case of mercury is rendered difficult by the complexities of the heavily-absorbed lines of the first and second subordinate series. Cadmium lines which are comparatively simple would be more suitable for this purpose.

The curve in fig. 7 relating p with $\xi\,(A_0 l)$ shows that the distance between the plates, p, at which the fringes cease to be visible diminishes rapidly with increase of ξ for points on the curve for which ξ is small, and as we move to the right, *i. e.* when ξ is large, this rate of diminution becomes very low. This means that, if the coefficient of absorption is large, a few centimetres of the radiating column are enough to cause considerable falling-off of the limiting order of interference at which the fringes cease to be discernible. The above considerations suggest that in experiments carried out with the object of determining the masses of radiating particles by visibility experiments, such as those of Buisson and Fabry, the use of an end-on tube should be avoided as likely to give too low a value for the mass of the luminous centres if the line radiation used for the purpose is appreciably absorbed by the luminous vapour.

Experimental values for the limit of interference $\frac{2p}{N} = N$ are slightly lower than the calculated ones, and the discrepancy is explained on the supposition that the temperature of the gas is slightly higher than that of the containing tube. Where end-on tubes have been used, part of this discrepancy at any rate may be attributed to the cause we have been discussing. Knowing the mass of the luminous centre and the limit of interference N, we can calculate from equation (10) the temperature of a thin layer of radiating gas. If the same equation is used to calculate the temperature of a long column, the calculated temperature may be far in excess of the true temperature, as equation (10) takes no account of the widening due to the length of the column. Taking the second case in Table IV. for $\xi=1$, a radiating column only 2·5 cm. long whose coefficient of absorption is 0·4 per cm. would give an experimental value of 612° absolute for the temperature of the vapour, whereas a thin layer would only give 400° absolute. If we take the sixth case, where the length of the radiating column is increased to 100 cm. under the same conditions of electrical excitation, the fictitious temperature works out to be 2540°.

IV.

A very interesting application of interference methods has been made by Buisson, Fabry, and Bourget* to the determination of the temperature of the Orion nebula and the masses of the luminous centres which give the lines attributed to nebulium, the hypothetical element supposed to be present in nebulæ. The method consists in producing Fabry and Perot interference-fringes on the image of the nebula in a telescope by means of a suitably placed Fabry and Perot etalon, and taking a series of photographs of the nebula with gradually increasing distances between the plates of the interferometer, the radiation used being the hydrogen line H_γ. This limit of interference and that found for the same line in the laboratory are used in determining the temperature of the nebula. Representing by N_l and N_n the limits for the radiations from a laboratory source and the nebula respectively, and by θ_l and θ_n the corresponding temperatures, we have

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* The Astrophysical Journal, xl. pp. 241-258.

$$N_l = \alpha \sqrt{\frac{M}{\theta_l}}, \qquad N_n = \alpha \sqrt{\frac{M}{\theta_n}};$$

$$\therefore\ \theta_n = \left(\frac{N_l}{N_n}\right)^2 \theta_l.$$

Here it is taken that the distribution of intensity in the radiated line in both cases is that of the radiation from a thin layer and of the form $e^{-k(\lambda-\lambda_0)^2}$. Even though the gaseous material of the nebula is at a very low pressure, the widening due to absorption owing to the enormous thickness of the radiating matter may be considerable. In the case of the hydrogen line of the Balmer series, an absorption has been detected and measured by several observers. Jungjohan * finds that in one of his experiments the absorption in the case of H_α and H_β was 100 per cent. with a layer of 6 cm. An extreme instance of the enormous influence which this widening may have on the observed temperature is provided by the mercury-arc discharge considered (see Table IV.). When $A_0 l = 3$, *i.e.* when the length of the radiating column is 7·5 cm., the limit of interference under the conditions of excitation cited above is $\cdot 63 \times 10^6$, whereas for a thin layer it is $1{\cdot}01 \times 10^6$. Using this tube end on would give 1120° absolute for the temperature of the vapour, whereas the correct temperature as judged by the limit of interference obtained with a thin layer as source of the radiation would be 400° absolute.

A column one metre long, as already stated, would give an estimated temperature of 2540° absolute. In the case of hydrogen the absorption coefficient is small, and probably is considerably less than in the case of the mercury-arc discharge, but enormous thickness of the radiating matter in the case of nebulæ may make up for the possible low value of the absorption coefficient. The uncertainty of the extent of widening due to absorption considerably diminishes the reliance to be placed on determinations of nebular temperatures by interference methods.

Buisson, Fabry, and Bourget remark that 15,000° the temperature of the nebula calculated from their observations, is a maximum, every other cause tending to lower this value

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* *Zeitschr. Wiss. Phot.* ix. (Oct., Nov., Dec. 1910)

But the present discussion indicates that the true temperature of the nebula may be far lower than 15,000°. If $A_0 l$ is of the order of 40, the temperature falls down to 2350°. For if θ_0 is the true temperature of the gas and θ the fictitious temperature calculated without taking into account the effect of absorption in the radiating column, we have from (10)

$$\frac{\theta_0}{\theta} = \left(\frac{N}{N_0}\right)^2,$$

where N_0 and N are respectively the limiting orders of interference for the long-column radiation and the radiation from a thin layer of the same gas. If $A_0 l = 40$, $\frac{N}{N_0} = \cdot 396$ (see Table IV., column 3); and taking the fictitious temperature to be 15,000°, we have for the true temperature

$$\theta_0 = \cdot 396^2 \times 15{,}000 = 2352^\circ \text{ absolute.}$$

A gas column 1000 kilometres long, with a coefficient of absorption $\cdot 4 \times 10^{-6}$ per cm., is sufficient to give this result. The discovery of dark irregular nebulæ and the resemblance existing between the spectra of bright irregular nebulæ and the spectra of stars involved in them have recently influenced astrophysicists in holding the view that irregular nebulæ are not self-luminous, but that the luminosity is due to the high-temperature stars associated with them. A low temperature for the nebula is consistent with this view. The almost invariable presence of B-type stars near a bright nebulous region and the absence of bright nebulæ near red stars, strongly suggest that the luminosity of the gaseous material of nebulæ, like the Orion nebula, is due to photoelectric excitation and electronic impact produced by high-frequency radiation and electron emission from the high-temperature stars involved in the nebulæ.

What has been said of the temperature determination holds also for the determination of the masses of the luminous centres which give rise to the so-called nebulium lines 3726 Å, 3729 Å, and 5006 Å. Here the data for calculation are supplied by the limiting orders of interference in the case of H_γ and the lines of unknown origin. Equation (10) gives the relation

$$\frac{M_x}{M_H} = \left\{\frac{N_x}{N_H}\right\}^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where M_x and M_H are the masses of the luminous centres of the unknown element and of the hydrogen atom respectively, and N_x and N_H represent the corresponding limiting orders of interference. Equation (1), which takes account of the length of the radiating column, gives

$$\frac{N_x^2}{N_H^2} = \frac{\phi({}_x A_0 l)}{\phi({}_H A_0 l)} \cdot \frac{M_x}{M_H}, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where ${}_x A_0$ and ${}_H A_0$ represent respectively the absorption coefficients of luminous nebulium and hydrogen for the respective lines considered, and l is the length of the radiating column which is taken to be the same for the two lines. If we assume that these coefficients are equal, equations (18) and and (19) become identical. But this assumption is by no means warranted, for it is known that different lines behave differently with respect to absorption; for instance, in the case of a mercury-vapour lamp the coefficient of absorption is large for the lines of the first and second subordinate series of triplets, and comparatively small for other lines. Consequently the limiting order of interference would be much smaller in the case of the heavily-absorbed lines than in the case of the feebly-absorbed ones. If a thin layer is used this discrepancy does not arise, for

$$\underset{A\,l \to 0}{\mathrm{Lt}} \ \phi(A_0 l) = 1{\cdot}427.$$

Using equation (18), the authors cited above have come to the conclusion that there are two unknown elements in the nebula with atomic weights 3 and 2 respectively. In the light of recent facts, if it be admitted that there are no elements with atomic weights between 1 and 4, the low values 3 and 2 obtained by interference methods have to be accounted for by supposing that

$$\phi({}_H A_0 l) > \phi({}_x A_0 l).$$

Since $\phi(A_0 l)$ diminishes as A_0 increases, l remaining unaltered, the above inequality means that the absorption coefficients of the unknown elements for the lines used in the calculation are larger than the coefficient of luminous hydrogen in the nebula for H_γ.

Buisson and Fabry* by an ingenious interferometer method have measured the widths of some of the absorption lines in the solar spectrum.

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* *Loc. cit.*; also Astrophysical Journal, xxxi. p. 98 (1910).

TABLE V.

Radiation.	Temperature width at 6000°.	Observed width in solar radiation (Buisson & Fabry).
6563 Å (H_α)	·362	·960
4861 Å (H_β)	·270	·750
5896 Å (D_1)	·068	·160
5890 Å (D_2)		·175
Iron line at 4400 Å ...	·033	·070

They account for the observed width by assigning part of the widening to the temperature (6000°) of the solar reversing layer, and part to the influence of the pressure there. Basing their calculations on the pressure-shift of the lines towards the red end of the spectrum, they arrived at 6 atmospheres as the value of the pressure in the reversing layer. In a subsequent paper *, while re-discussing their results, they attribute the shift of the solar lines to the Einstein gravitation effects, and consider the pressure in the reversing layer to be low. Fowler and Milne (Monthly Notices Roy. Astr. Soc. lxxxiii. p. 416, 1923), from considerations of the intensities of spectral lines in stellar spectra based on the theory of high-temperature ionization, conclude that the pressure in the reversing layer is of the order of 10^{-4} atmos. (about 0·1 mm. of mercury). In the paper of Fowler and Milne there is a summary of the available astronomical evidence in support of the view that the pressure in the reversing layer is low, some of these estimates being as low as 10^{-6} atmos., *i. e.* about ·001 mm. of Hg. If it be granted that the pressure in the reversing layer is small—say of the order of 0·1 mm. of mercury,—that part of the widening which was originally attributed to the effect of pressure remains unexplained. To take a case discussed by Buisson and Fabry, the observed width of a solar iron line at 4470 Å is ·070 Å, while the calculated value, taking into account temperature only, is ·033 Å at 6000°. If the effect of pressure in widening the solar lines is ruled out, the additional widening (viz. ·037 Å) has to be traced to the influence of the depth of the reversing layer. The increase in the observed width of other solar lines, such as H_α and H_β of hydrogen and D_1 and D_2 of sodium (see Table V.), over and above what can be ascribed to temperature, has to be accounted for in a similar manner. It is of interest to note in this connexion that an increase to 1000 miles of the length of the radiating column of luminous mercury vapour, under conditions of excitation considered in the calculations embodied in this paper, increases the width of a heavily-absorbed line of the 5461 Å group only to ·028 Å.

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* *C. R.* clxxii. p. 1020 (1921).

The mercury reasonance line 2537 Å is easily reversed in a prism spectroscope on the continuous background of the spectrum of white light which has passed through unexcited mercury vapour at 60° C. At this temperature the temperature width of the lines at 2537 Å is too small for the reversal to be revealed in such a low resolving power arrangement as a prism spectroscope; but $A_0 l$, the product of the coefficient of absorption and the thickness of the absorbing layer (1 cm.) of normal mercury vapour at 60° C. (pressure ·02 mm.), is nearly 440, as may be calculated from the observation recorded by R. W. Wood that the intensity of the resonance radiation in mercury vapour at 20° C. (·001 mm. pressure) falls to 1/3 in a distance of 0·5 mm. This high value of $A_0 l$ has the effect of increasing the width of the absorption line; and if the line is complex and has very close satellites, the effective region of absorption is greatly increased as the absorption lines of such satellites widen out and fuse with the absorption line of the main component.

Description of Plate.

Spectrogram II. was taken when the pressure in the small lamp (fig. 5, ii.) was 3 mm. The arrow-head shows the position of the separating line between A and F. This separating line is absent in the long-column pattern I. (*b*). Spectrogram III. was taken with the pressure kept low in the long column (fig. 5, i.) by the use of a liquid-air-cooled charcoal tube. The difference in the appearance of patterns II. and III. is distinct, the lines in the long column pattern III. appearing fuzzy and widened. The arrow-heads in III. show the positions in two consecutive orders of the unresolved main line, which has suffered comparatively greater absorption by the luminous vapour cooled by the neighbouring air-blast directed against the bulb b_2 (fig. 5). I. *b* and III. are long column patterns.

V. *Absorption Spectrum of Potassium Vapour at High Temperatures.* *By* N. K. SUR, *M.Sc.*, *and* R. N. GHOSH, *M.Sc.*, *University of Allahabad**.

[Plate II.]

SAHA'S well-known theory of thermal excitation of elements at high temperatures states that as the temperature of a mass of gas is gradually increased the gas is at first capable of absorbing the wave-lengths belonging to the primary series characteristic of the element. As the temperature is further raised the primary lines are emitted. At this stage there will be some atoms for which the valency electrons will be in the orbit of next higher energy level than that of normal position. Such atoms are called excited atoms. With the rise of temperature, the proportion of neutral atoms, which are only capable of absorbing the lines of the primary series, diminishes, while those in the excited condition of next higher energy level, viz. in the $2p$ orbit, increase. At this stage the characteristic wave-lengths of the subordinate series are capable of being absorbed by the heated gas. The intensity of the absorption lines belonging to the subordinate series can be easily calculated from Fowler and Milne's † extension of Saha's theory. Let the numerals 1, 2 denote the possible stationary states of a given neutral atom, arranged in order of decreasing negative energy; the numeral 1 denotes the atom in its normal state. Let x_1, x_2 denote the energy of the levels, so that x_1 is the ionization potential, x_1-x_2 is the first resonance potential, etc. Further, let q_1, q_2 be the weights of corresponding states. Let x be the fraction of atoms ionized ; let P_e be the partial pressure due to electrons from all sources, and let σ be the number of valency electrons in the atoms in equivalent orbits, and let f_r be the fraction of neutral atoms in the rth state. Then f_r is given by the formula

$$f_r = q_r e^{-(x_1-x_2)\,k\mathrm{T}}/b\mathrm{T},$$

$$b(\mathrm{T}) = q_1 + q_2 e^{-\frac{(x_1-x_2)}{k\mathrm{T}}} + q_3 e^{-\frac{(x_1-x_3)}{k\mathrm{T}}}.$$

The fraction n_r of the total number of atoms which are neutral and in the *r*th state is given by

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* Communicated by Prof. M. N. Saha.

† Monthly Notices of Royal Astro. Soc. vol. lxxxiii.

$$n_r = f_r(1-x),$$

where x is the fraction ionized.

$$n_r = f'_r = q_r e^{-(x_1 - x_r)/kT} / b(T)$$

approximately. For monavalent atoms

$$q_1 = q_2 = \ldots\ldots = q_r = 1,$$

$$b(T) = 1,$$

$$f_r = e^{-\frac{h\nu}{kT}}.$$

Temp. absolute.	n_r.
700	4×10^{-12}
900	$2{\cdot}5 \times 10^{-9}$
1100	$4{\cdot}9 \times 10^{-8}$
1300	$9{\cdot}5 \times 10^{-7}$

This theory has been put to test at least qualitatively by King [*] for a number of elements. He heated the substance under examination in a tube-resistance furnace of carbon to temperatures of about 3000° C. The absorption of the lines of the subordinate series by potassium vapour has been obtained by Narayan [†] by heating potassium in a steel tube raised to a high temperature by surrounding it with wire of suitable material and carrying electrical current. He also used Bunsen burners simultaneously to facilitate the increase of temperature. In view of the necessity for pure thermal excitation of the atoms, the experiment on potassium vapour has been repeated by heating it in a steel tube in a coal furnace described below.

Experiments on Potassium Vapour.

One of the earliest experiments on the absorption of potassium vapour is due to Bevan [‡]. He recorded the absorption of the principal series in the ultra-violet down to the seventeenth number and observed the absorption bands

[*] Astrophysical Journal, lv. pp. 380-390 (1922).

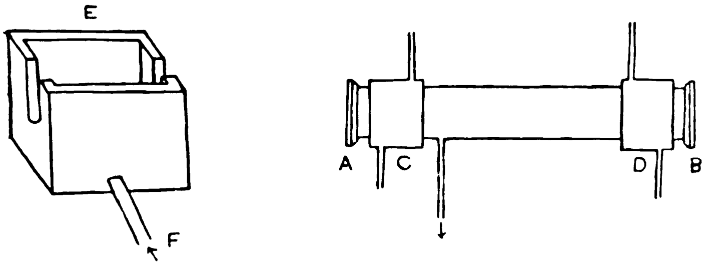
[†] Narayan and Gunnayya, Phil. Mag. xlv. pp. 831-834.

[‡] Proc. Phys. Soc. London, 1910; and Proc. Roy. Soc. lxxxiii. (1910).

in different parts of the spectrum, to which reference will be made later on. A more complete study of the principal series has been made by Datta *. The method adopted to obtain the reversal of the lines of the subordinate series is to vaporize the metal in an iron tube 40 cm. long and 3 cm. in diameter, as shown in figure 1.

The ends A and B were closed with plate glass sealed in brass sockets screwed to the ends of the tube. The joints were made air-tight by sealing-wax. To keep the ends cool, cold water was kept circulating through two outer jackets of brass C and D near the ends of the tube. The central portion of the tube containing the metal was heated strongly by surrounding it with a rectangular oven E made of clay and of suitable dimensions, through the end faces of which the tube could pass snugly, the top of the oven being kept open for introducing coal. One of the side faces of the oven was fitted with a brass tube F, through which a strong blast of air could be admitted from a blower. By this means sufficiently high temperatures could be attained quickly. In fact, the temperature was high enough to melt the iron tube. To start with, the tube was always carefully exhausted by a Gaede oil-pump. If desired, the tube could be put in communication with the pump during the course of experiment. The source of light was a fifty candle-power point-o-lite lamp, and the spectrum was photographed on panchromatic plates in the first-order spectrum of a five-foot concave grating of dispersion 11·128 per mm. The wave-lengths were measured by means of a comparative spectrum of iron.

Fig. 1.



As soon as heating is begun dense vapour is formed, and the incident light is totally cut off. When the temperature of the tube is raised to 500° C. the colour of the transmitted

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* Proc. Roy. Soc. ci. pp. 539–547 (1922).

light is green, and at the temperature of red heat the colour changes to bluish green. At this second stage no absorption line is observed in the visible region, but the spectrum is traversed by a number of channelled absorption bands. At the third stage, when the temperature is further increased, the absorption bands become more complicated and they are accompanied by one or two absorption lines scarcely visible on the plates. When the inner walls of the tube were raised to yellow heat a number of sharp absorption lines were obtained, and this state was found to be most suitable for obtaining reversals of lines of subordinate series. The temperature attained was about 1300° C., above which the iron tube melted. The following absorption lines were obtained :—

Series notation.	m.	λ (Å.U.).
$2p-ms$	4	5802 5783
,,	5	5340 5323
,,	6	5099 5084
$2p-md$	7	5112 5097

In addition to these, the following absorption lines were also obtained at high temperatures, but they could not be identified with known lines of potassium nor could they be allotted to any series relation. It may be noted here that some new lines have also been recorded by Datta [*].

λ (Å.U.).
5225
5212
5206
5186
5167
5155
5136

The line $\lambda=4641$ $(1s-2d)$ was easily obtained on all the plates. That this is an exception to the principle of selection of Bohr has already been pointed out by Foote and Mohler [†] and by Datta [‡]. The occurrence of the line in the present case where no external electric field is present supports their views.

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[*] *Loc. cit.*

[†] Phil. Mag. xliii. (1922).

[‡] *Loc. cit.*

Bands.

The presence of channelled bands in the absorption spectrum of potassium vapour has been noticed previously by Bevan * and Narayan †. Bevan noticed channelled bands in three distinct regions, (A) red, (B) orange-green, and (C) blue-violet. The edges of these absorption bands are regions of greater absorption and lie towards the violet. As in the case of the line spectrum the channelled bands also undergo variation with rise of temperature. First the bands of the red region appear in absorption, next, the bands in the blue-violet region, and lastly the bands in the orange-green region are obtained. These bands are clearly seen at low temperature (about 600° C.), but at higher temperature (about 1000° C.) they diminish in intensity. At intermediate temperatures the channelling tends to disappear and merges into wide bands. This is shown for the case of bands in the orange-green region in figs. 2 and 3 (Pl. II.). The D lines of sodium appear as impurity. Some measurements have been recorded both by Bevan and Narayan for the wave-lengths of the heads of the bands in the red region, but none of them has given any measurement for the bands in the other regions. A list of wave-lengths of the heads of the channelled bands in the orange-green region is recorded below.

No.	λ (Å.U.).
1	6024
2	6001
3	5979
4	5957
5	5923
6	5914
7	5870
8	5846
9	5824
10	5804
11	5784
12	5766
13	5746
14	5729
15	5714
16	5699
17	5682

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* *Loc. cit.*

† *Loc. cit.*

VI. *On the Depth of Earthquake Focus.* *By* SUDHANSU KUMAR BANERJI, *D.Sc., Director, Bombay and Alibag Observatories* *.

EVER since the late Dr. G. W. Walker † made the startling suggestion that the depth of earthquake focus is of the order one-fifth of the earth's radius, or about 1250 km., the subject has excited a great controversy ‡. It is not my intention in the present paper to enter into this controversy, or to discuss the accuracy of the values of the emergence angle of P waves measured at Pulkovo on which Walker relied for his conclusion. My object is to point out certain consequences of assuming a considerable depth for the focus on the different phases in the seismogram and to ask whether, in view of these consequences, it is reasonable to consider the focus to be very deep-seated. When the focus is very deep, any disturbance that starts there cannot at once initiate the surface waves. It can only give rise to three-dimensional longitudinal and transverse waves, which will travel to the observing station either by a single brachistochronic path or by several brachistochronic paths, after undergoing one or more reflexions at the earth's surface or in the heterogeneous mass of rocks constituting the earth's crust. The arrivals of all these waves are identified in the seismograms, and are designated as P, S, PR_1, PR_2, etc.; SR_1, SR_2, etc.; SP, PS, etc., waves. If the observing station is at a great distance from the focus it is not of much consequence, so far as the intensity of these waves is concerned, whether the depth of the focus is 100 km. or 1250 km., for the intensity will depend on the lengths of the brachistochronic paths. The maximum difference that is possible between the lengths of the brachistochronic paths which these waves will take to reach a very distant observing station, from two foci, one on the surface and the other at an internal point on the same diameter, is equal to the distance between the two foci. Consequently, even when the depth of the second focus is 1250 km., the amplitudes of the P or S waves received at a station very near the antipodes from the two foci will differ by a small quantity from each other.

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* Communicated by the Author.

† Phil. Trans. Roy. Soc. A, ccxxii. pp. 45-51 (1921).

‡ See, for instance, a note by the present writer in 'Nature,' Jan. 26, 1922; the Report of the discussion on the depth of earthquake foci held at the Meeting of the Royal Astronomical Society, March 3, 1922 ('The Observatory,' April 1922); and the Twenty-seventh Report of the Committee of Seismological Investigations, British Association, Hull, 1922.

This is, however, not the case with Rayleigh waves. Had the earth been an unlimited elastic solid, there would have been no surface reflexion and also no production of Rayleigh waves. But the earth has a spherical boundary, and consequently the portion of its surface known as the epicentral tract—that is to say, the region lying vertically over the internal focus—will be the first to be affected by the arrival of the longitudinal and transverse waves originated there. The disturbance in the epicentral tract will be maximum compared with the other parts of the earth's surface, the region being nearest to the focus, and will act as a secondary source for the production of surface waves. If it is then admitted that a part of the energy carried away by the longitudinal and transverse waves is transformed into surface waves on these waves reaching the surface, there is no reason to consider that the production of the surface waves would be confined to the epicentral tract alone, although no doubt the largest effects will be produced there. This is probably the reason why the long wave phase in the seismogram is a prolonged disturbance and is followed by a coda lasting for hours, particularly in the case of great tectonic earthquakes. The amplitudes of the longitudinal and transverse waves at any point in the epicentral tract will vary as inverse powers of the distance of the point from the focus. The depth of focus has therefore a considerable influence on the production of surface waves.

All records of distant earthquakes, if these have not been vitiated by the imposition of the free periods of the horizontal pendulum in the recording instrument, show that the amplitude of the long wave phase is generally much larger than the amplitudes of the other phases. This is what we should expect, because the surface waves being two-dimensional must acquire at a great distance from the source a continually increasing preponderance over the other waves. If, therefore, the effect of a considerable depth of focus on the production of Rayleigh waves is so great as to make the long wave phase in the seismograms at large epicentral distances merge into insignificance compared with P and S phases, then the hypothesis of a very deep focus will obviously have to be abandoned. I proceed, therefore, to investigate the effects of various focal depths on the relative importance of the different phases in the seismograms.

In the mathematical treatment of this problem, the source of disturbance has to be assumed to be of a specified type, but may be assumed to be situated at any depth below the earth's surface. In an actual earthquake the source is not of the ideal type we represent by the usual mathematical forms. Even with simplified assumptions regarding the source, the mathematical difficulties in obtaining complete solutions of the elastic equations of motion consistent with the boundary condition, which is one of zero stress at the earth's surface, are very great. The displacements at any point on the earth's surface deduced from the solutions thus obtained agree, however, in their main features with the displacements recorded by seismographs. The effect of the complex nature of an earthquake source is mainly to introduce complexities in the character of the waves of the different phases in the seismograms and to prolong the disturbance in each phase, but not to alter the essential features by which these phases are recognized in the seismograms. No doubt, if the earthquake be supposed to originate at a fault, the mass movement there may be horizontal, inclined, or vertical, or of the nature of a twist; and this mass movement may influence one type of waves more than the others, and the energy sent out in different azimuths and at different vertical angles may be dependent on the direction of the fault and on the nature of the mass movement. But the law of divergence holds, and the two-dimensional waves always gain a continually increasing importance with distance over the three-dimensional waves, unless there are factors which make the immediate production of the two-dimensional waves impossible, and make them dependent for their initiation on the arrival of the three-dimensional waves at the surface.

2. *Seismic Waves due to a Source situated at the Earth's Surface.*

In order that any purely theoretical consideration can be made applicable to form an estimate of the depths of earthquake foci, it is essential first to prove that the kind of motion we obtain at any point on the earth's surface due to a single impulse of a specified type situated on the surface of the earth agrees in its main features with those observed in an earthquake. When this general similarity has been proved, we can then examine what happens when the focus is situated at a definite depth below the surface.

In a well-known paper published in the 'Philosophical Transactions of the Royal Society,' A, cciii. (1904), Professor Horace Lamb has investigated the propagation of tremors over the surface of a semi-infinite elastic solid. He takes the source of disturbance to be a single arbitrary impulse of the type

$$R(t) = \frac{\overline{R}}{\pi} \frac{T}{t^2 + T^2},$$

situated at a point on the earth's surface, t denoting the time, T the duration of impulse, and $\overline{R}$ a constant. This expression means that the pressure at the source changes from one constant value to another according to the law

$$A + B \tan^{-1} \frac{t}{T},$$

where A and B are constants. The disturbing pressure has no definite epoch of beginning or ending, but the range of time within which it is sensible can be made as small as we please by diminishing T.

The horizontal and vertical displacements of the ground due to a single impulse of this type have been calculated by Professor Lamb in pp. 37–40 of the paper above referred to, and the whole progress of these displacements has been plotted on p. 40. These show that as the wave system passes any point of the earth's surface, the horizontal displacement shows first of all a single well-marked oscillation on the arrival of the longitudinal waves (P). This is followed by a period of comparative quiescence, and then another oscillation corresponding to the epoch of arrival of transverse waves (S). The whole of this stage constitutes what is called the "minor tremor"; it is, of course, more and more protracted the greater the distance from the source, and its amplitude continually diminishes not only absolutely, but also relatively to that of the "main shock", which is identified with the arrival of the Rayleigh waves. Similar statements apply to the vertical displacements.

These results have been obtained for a semi-infinite elastic solid bounded by a plane, and cannot strictly apply to a spherical body like the earth. But then, if we confine our attention to the two principal waves P and S arriving at the station direct from the focus as well as the Rayleigh waves travelling over the earth's surface from the epicentral tract, and ignore for the present all waves which arrive at the station after undergoing a single or multiple reflexions and are recognized in the seismograms by the notation PR_n, SR_n, S_mP_n, P_nS_m, ($n=1, 2 \ldots$, $m=1, 2 \ldots$), the *chief qualitative* *difference* introduced by the curvature of the earth would be that P and S waves would be (at distances comparable with the earth's radius) accelerated relatively to L. On account of the shorter routes along which the P and S waves will now have to travel, they will be a little more pronounced compared with L.

A comparison with the broad features of actual seismograms at large epicentral distances will make it clear that the figures given by Prof. Lamb on p. 40 of his paper give a reasonable representation of the effects due to a single impulse. The long wave phase appears to be a little more pronounced compared with the P and S phases than in actual seismograms at great distances, and this may partly be due to our neglecting the curvature of the earth and the source being supposed to be situated on the surface, and partly to the usual high preponderance of Rayleigh waves over the longitudinal and transverse waves when dissipation due to viscosity and other factors is neglected.

3. *Seismic Waves due to a Source situated at a Depth (f) below the Earth's Surface.*

The source of disturbance may now be supposed to be situated at a depth f below the earth's surface. The origin of coordinates is supposed to be situated on the surface, the z-axis passing through the focus and the plane boundary coinciding with $z=0$. The form to be chosen for the source must be of a type which is possible in an elastic solid. Assuming first that the motion is simple harmonic (e^{ipt}), the elastic equations of motion are satisfied by

$$u=\frac{\partial\phi}{\partial x}+\frac{\partial^2\chi}{\partial z\,\partial x},\quad v=\frac{\partial\phi}{\partial y}+\frac{\partial^2\chi}{\partial y\,\partial z},\quad w=\frac{\partial\phi}{\partial z}+\frac{\partial^2\chi}{\partial z^2}+k^2\chi, \quad . \; . \; . \quad (1)$$

where u, v, w denote the components of velocity at any point, and ϕ and χ are given by

$$(\nabla^2+h^2)\phi=0,\qquad(\nabla^2+k^2)\chi=0,\quad . \; . \quad (2)$$

where

$$h^2=\frac{p^2\rho}{\lambda+2\mu}=p^2a^2,\qquad k^2=\frac{p^2\rho}{\mu}=p^2b^2,\quad . \; . \quad (3)$$

ρ denoting the density, and λ, μ the usual elastic constants, a, b the *reciprocals* of the wave velocities corresponding to the irrotational and equivoluminal types of disturbance respectively. The source of disturbance at the point

$(0, 0, f)$, distance f below the earth's surface, may therefore be assumed to be of the type

$$\phi = \frac{e^{-ihr}}{r}, \quad \chi = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

r denoting the distance from this point.

The values of ϕ and χ at any point have then to be obtained consistent with a source of this type and the condition of zero stress on the plane boundary. This has been done by Prof. Lamb. The horizontal and vertical displacements at any point on the earth's surface are calculated by (1), and these are given by

$$q_0 = 4\int_0^{\infty} \frac{k^2\xi^2\beta}{F(\xi)} e^{-\alpha f} J_1(\xi\varpi)\, d\xi, \quad . \quad . \quad . \quad (5)$$

$$w_0 = -2\int_0^{\infty} \frac{k^2\xi(2\xi^2-k^2)}{F(\xi)} e^{-\alpha f} J_0(\xi\varpi)\, d\xi,$$

where

$q_0 =$ horizontal displacement, $w_0 =$ vertical displacement,

$\alpha^2 = \xi^2 - h^2$, $\beta^2 = \xi^2 - k^2$, $\varpi = \sqrt{(x^2+y^2)}$, and

$$F(\xi) = (2\xi^2-k^2)^2 - 4\xi^2\alpha\beta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For a detailed analysis of this case, reference is made to Prof. Lamb's paper (pp. 33–36).

These are the complete expressions for the horizontal and vertical displacements at any point on the earth's surface, and comprise within themselves all the different phases of seismograms. In order, therefore, to fully interpret these integrals, these have to be broken up into terms of different orders of magnitude.

The generalization of these results so as to apply to an arbitrary time variation of the source, as has been pointed out by Lamb, follows much the same course as in article 9 of his paper. But so far as the effect of depth on the relative amplitudes of the three principal phases is concerned, the type of the source is probably not of much consequence.

In order to understand fully what the expressions (5) mean, we may enter into a little more detail.

If we assume the existence of an equal source at the image point $(0, 0, -f)$, and denote distance from this point by r', and take

$$\phi = \frac{e^{-ihr}}{r} + \frac{e^{-ihr'}}{r'}, \quad \chi = 0, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

then these expressions will account for all the reflexions of longitudinal and transverse waves that occur on account of the existence of a bounding surface. But these do not satisfy the condition of zero stress on the boundary. Now, in the neighbourhood of the plane $z=0$,

$$\phi = \int_0^\infty \frac{e^{-\alpha(z+f)}}{\alpha} J_0(\xi\varpi)\xi\,d\xi + \int_0^\infty \frac{e^{\alpha(z-f)}}{\alpha} J_0(\xi\varpi)\xi\,d\xi$$

$$= \int_0^\infty \frac{\cosh \alpha z}{\alpha} e^{-\alpha f} J_0(\xi\varpi)\xi\,d\xi. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Consequently, if $[p_{zz}]_0$ and $[p_{z\varpi}]_0$ denote the vertical component of the stress and the component of the stress in any horizontal direction respectively on this plane, we have

$$[p_{zz}]_0 = 2\mu \int_0^\infty \frac{(2\xi^2-k^2)}{\alpha} e^{-\alpha f} J_0(\xi\varpi)\xi\,d\xi, \quad . \quad . \quad (9)$$

$$[p_{z\varpi}]_0 = 0.$$

In order, therefore, to annul the stresses on the plane $z=0$, we have to assume the existence of a system of negative vertical stresses of the type

$$-2\mu \frac{2\xi^2-k^2}{\alpha} e^{-\alpha f} J_0(\xi\varpi)\xi\,d\xi \quad . \quad . \quad . \quad (10)$$

distributed over the plane, find out the displacements corresponding to these latter stresses, and then integrate with respect to ξ from 0 to ∞. The displacements * at any point on the surface due to this distribution of stresses are

$$q_0 = \int_0^\infty \frac{\xi(2\xi^2-k^2-2\alpha\beta)}{F(\xi)} \cdot \frac{2\xi^2-k^2}{\alpha} e^{-\alpha f} J_1(\xi\varpi)\xi\,d\xi,$$

$$w_0 = -2\int_0^\infty \frac{k^2(2\xi^2-k^2)}{F(\xi)} e^{-\alpha f} J_0(\xi\varpi)\xi\,d\xi. \quad . \quad . \quad . \quad (11)$$

These, when added to the displacements derived from (7), give the complete expressions already given in (5) for the displacements at any point on the earth's surface consistent with the type of source assumed and the condition of no stress on the boundary.

We now understand the genesis of the Rayleigh waves. Mere reflexions at the bounding surface of the waves generated at the internal source do not explain the whole phenomenon. Something more is required to satisfy the conditions which must hold at a free surface. The satisfaction

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* See p. 32 of Prof. Lamb's paper.

of these conditions requires the imposition of a properly distributed system of stresses at the boundary surface, the imposed stresses accounting for the production of surface waves.

5. *Effect of the Depth of Focus on the Rayleigh Waves.*

We now proceed to an analysis of the complete expressions (5) for the displacements at any point on the surface due to an *internal* source situated at a depth f below the surface, and to an examination of the effect of depth on the amplitude of Rayleigh waves.

The parts * of q_0 and w_0 which are most important are

$$\left.\begin{aligned} q_0 &= -\frac{4\pi k^2\kappa\beta_1}{F'(\kappa)} e^{-\alpha_1 f} D_1(\kappa\varpi) e^{ipt} + \text{etc.}, \\ w_0 &= \frac{2\pi k^2\kappa}{F'(\kappa)} (2\kappa^2 - k^2) e^{-\alpha_1 f} D_0(\kappa\varpi) e^{ipt} + \text{etc.}, \end{aligned}\right\} \quad . \quad (12)$$

where κ is a root of the equation $F(\xi)=0$; that is,

$$1 - 8\frac{\xi^2}{k^2} + \left(24 - 16\frac{h^2}{k^2}\right)\frac{\xi^4}{k^4} - 16\left(1 - \frac{h^2}{k^2}\right)\frac{\xi^6}{k^6} = 0, \quad . \quad (13)$$

and α_1, β_1 are given by

$$\alpha_1{}^2 = \kappa^2 - h^2, \qquad \beta_1{}^2 = \kappa^2 - k^2.$$

At a great distance ϖ, we have

$$\left.\begin{aligned} q_0 &= \frac{4\pi i k^2\kappa\beta_1}{F'(\kappa)} e^{-\alpha_1 f} \sqrt{\frac{2}{\pi k\varpi}}\, e^{i(pt-\kappa\varpi-\frac{1}{4}\pi)}, \\ w_0 &= \frac{2\pi k^2\kappa(2\kappa^2 - k^2)}{F'(\kappa)} e^{-\alpha_1 f} \sqrt{\frac{2}{\pi k\varpi}}\, e^{i(pt-\kappa\varpi-\frac{1}{4}\pi)}. \end{aligned}\right\} \quad . \quad (14)$$

We easily identify that these expressions represent the displacements due to Rayleigh waves. It is important to notice the occurrence of the factor $e^{-\alpha f}$ in these expressions. This represents the effect of the depth of the focus. The amplitude is seen to diminish with increasing distance according to the usual law $(\varpi^{-\frac{1}{2}})$ of annular divergence.

The influence of the factor $e^{-\alpha f}$ on the amplitude of the Rayleigh waves may now be examined in detail. If the material of the earth be supposed to satisfy Poisson's condition between the elastic constants, namely $\lambda = \mu$, then $h^2 = \frac{1}{3}k^2$. The cubic equation (13) then has all its roots real.

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* See p. 36 of Lamb's paper, expressions (161).

It has been shown by Rayleigh that only one of these three roots gives rise to real Rayleigh waves. This root is

$$\frac{\kappa}{k} = 1{\cdot}087664\ldots .$$

We have then

$$\alpha_1^2 = \kappa^2 - h^2 = \left[\left(\frac{\kappa}{k}\right)^2 - \frac{1}{3}\right] k^2$$

$$= \left[(1{\cdot}088)^2 - \tfrac{1}{3}\right] k^2 = (0{\cdot}92k)^2.$$

Therefore

$$\alpha_1 = 0{\cdot}92k = 0{\cdot}92 \times \frac{2\pi b}{T},$$

where T = the period of Rayleigh waves, mainly 12 seconds and 20 seconds, and

$\frac{1}{b}$ = the velocity of propagation of transverse waves
= 4 km. per second.

Taking T = 12 seconds, we find $\alpha_1 = 0{\cdot}12$,
and T = 20 seconds, we find $\alpha_1 = 0{\cdot}08$.

We therefore take α_1 to be roughly equal to $\frac{1}{10}$.

If, now, A denotes the amplitude of the Rayleigh waves recorded at any station, produced by an earthquake the focus of which is situated on the surface, then, when the focus is

(1) 10 km. deep, the amplitude = Ae^{-1},
(2) 100 km. deep, the amplitude = Ae^{-10},
(3) 1000 km. deep, the amplitude = Ae^{-100},

the sources being supposed to be of the same intensity and all in the same vertical line. Since $e = 2{\cdot}72$ nearly, the amplitude of the Rayleigh waves undergoes a very rapid diminution indeed with increasing depth of the focus.

5. *Effect of the Depth of Focus on the* P *and* S *Waves.*

It has already been pointed out that the most important terms in the complete expressions (5) for the displacements of any point on the surface are those numbered (12). The general form and the order of magnitude of the residual disturbance have also been obtained by Lamb* when $h\varpi$ and $k\varpi$ are large, ϖ denoting as usual the distance from the axis. The lowest order terms depending on $\frac{1}{k\varpi}$ in the residual expressions for q_0 and w_0 are of the types

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* See p. 36 of his paper.

$$\frac{e^{ipt}}{(k\varpi)^{\frac{3}{2}}}\int_0^{\infty}\frac{e^{-ik\varpi\cosh u}}{(\cosh u)^{\frac{1}{2}}}du \quad \text{and} \quad \frac{e^{ipt}}{(k\varpi)^{\frac{3}{2}}}\int_0^{\infty}\frac{e^{-ik\varpi\cosh u}}{(\cosh u)^{\frac{3}{2}}}du.$$

By considering the asymptotic expansion of these integrals, Prof. Lamb has shown these to be ultimately comparable with

$$e^{ip(t-b\varpi)}/(k\varpi)^2,$$

which therefore represents the most important term in the transverse waves (S). In the same way the terms in q_0 and w_0 which correspond to the longitudinal waves are ultimately comparable with

$$e^{ip(t-a\varpi)}/(k\varpi)^2.$$

The depth of the focus does not enter into these expressions, but the amplitude diminishes inversely as the square of the distance from the source. This is simply because there is a boundary. Had the elastic waves simply diverged from a centre in an unlimited medium, the amplitude would have varied inversely as the distance.

It is not difficult to understand why the effect of the depth of focus on the P and S phases at large epicentral distances (large compared with the focal depth) is negligible. Whenever there is a boundary, the law of divergence for the P and S waves is always the inverse square of the distance. Since the maximum difference possible between the distances of an observing station from a focus situated on the earth's surface, and one at a depth f below, is the distance between the foci, the maximum value of the ratio of the amplitudes of the P or S waves arriving at the station from the two foci (supposed to be of equal strengths) is

$$\frac{\varpi^2}{(\varpi-f)^2}=1+\frac{2f}{\varpi}=1, \quad \text{approximately},$$

in all cases where $\frac{f}{\varpi}$ can be regarded as small.

6. *Possible Depths of Earthquake Foci.*

In the seismograms we have a ready means of determining the relative amplitudes of the different phases. The records of all aperiodic seismographs for distant earthquakes definitely show that the amplitudes of the L phase are much greater than those of the P and S phases. If, therefore, we can prove that when the focus is 1000 km. deep (say) the seismogram at a distant observing station ought to show the amplitude of the L phase to be much smaller than those of the P and S phases, then, this being contrary to the facts, we must conclude that 1000 km. is too large a depth for the focus.

Let us take an extreme case, but a typical one. Suppose that there are two sources of disturbance of equal strengths, one at the earth's surface and the other at a depth of 1000 km. Let the observing station be at a distance of 20,000 km. measured circumferentially from the first focus—that is to say, very near the antipodes, the earth's radius being 6500 km. (say). If we are permitted to regard the sources as simply point-sources, and if we suppose that the amplitudes of P, S, and L waves produced by the surface source at unit distance (here 1 km.) from it are all the same and equal to A (say), then the amplitudes of these waves at the observing station will be

$$\frac{A}{(13,000)^2}, \qquad \frac{A}{(13,000)^2}, \qquad \frac{A}{(20,000)^{\frac{1}{2}}}$$

respectively, P and S waves being supposed to have travelled by straight paths passing almost through the earth's centre.

This means that although at a distance of 1 km. the amplitudes of all these waves were the same, when these waves have reached the observing station, the amplitudes of the L waves are about 12×10^5 times greater than the amplitude of the P or S waves.

The amplitudes of the waves received from the second focus will, on the other hand, be

$$\frac{A}{(13,000-1000)^2}, \qquad \frac{A}{(13,000-1000)^2}, \qquad \frac{Ae^{-100}}{(20,000)^{\frac{1}{2}}}$$

respectively. That is to say, the conditions are now reversed, and the amplitudes of the P or S waves are $2{\cdot}688 \times 10^{37}$ times greater than the amplitudes of the Rayleigh waves. It is inconceivable that there is any factor we have ignored which can restore this enormous reduction of the amplitudes of the Rayleigh waves and make them larger than the amplitudes of the P or S waves. A depth of 1000 km. is therefore impossible for an earthquake focus.

If the depth of the second focus is only 100 km., the amplitudes of the P, S, and L waves at the observing station will be

$$\frac{A}{(13{,}000-100)^2}, \qquad \frac{A}{(13{,}000-100)^2}, \qquad \frac{Ae^{-10}}{(20{,}000)^{\frac{1}{2}}}$$

respectively.

This makes the amplitude of the Rayleigh waves about 55 times greater than the amplitude of the P or S waves. 100 km. is therefore a possible depth for an earthquake focus.

A focal depth of 200 km. will make the amplitude of the Rayleigh waves received at the observing station about $\frac{1}{400}$ of the amplitude of either P or S waves. A depth of even 200 km. will therefore appear to be too large an estimate for the earthquake focus.

7. *Discussion of the Problem when the Earth is assumed to be Spherical.*

In a recent paper Jeans[*] has discussed the problem, particularly in certain of its aspects which seem to have a direct seismological importance, of the vibrations of an elastic sphere in which the mutual gravitational attraction of the parts is taken into account as well as the variation of the physical constants of the earth's material with distance from the centre. The free vibrations are deducible from the functions of the type

$$\left.\begin{aligned} P &= F_1(r)S_n(\theta, \phi) \cos pt, \\ w' &= f_1(r)S_n(\theta, \phi) \cos pt, \end{aligned}\right\} \text{ (Primary vibrations)},$$

$$S = F_2(r)S_n(\theta, \phi) \cos pt, \qquad \text{(Secondary vibrations)},$$

where $S_n(\theta, \phi)$ is a surface harmonic of degree n, and $F_1(r)$, $f_1(r)$, $F_2(r)$ satisfy certain differential equations with respect to r. A natural earthquake shock can be regarded as being made up in great part of free vibrations in which the order n of the surface harmonic is large, which is tantamount to neglecting all earthquake waves except those of wave-length short in comparison with the earth's radius. With this assumption the solution for S, throughout any small range of values of r in the neighbourhood of $r=a-f$, can be written in the form

$$S = B \exp. \left[-r \left\{ n(n+1) \left(\frac{1}{(a-f)^2} - \frac{1}{a^2} \right) \right\}^{\frac{1}{2}} \right] \times \cos \left\{ [n(n+1)]^{\frac{1}{2}} \theta \pm pt \right\},$$

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[*] Jeans, Proc. Roy. Soc. A, cii. pp. 554-574 (1923).

where

$$p=\frac{1}{a}\sqrt{\left[n(n+1)\frac{\mu}{\rho}\right]},\quad a=\text{earth's radius},\quad f=\text{focal depth},$$

the focus being supposed to be situated on the radius $\theta=0$. This can also be written in the form

$$S = B\,\text{exp.}\Bigl[-\frac{r}{a}\left\{2n(n+1)\frac{f}{a}\right\}^{\frac{1}{2}}\cos\{[n(n+1)]^{\frac{1}{2}}\theta \pm pt\},$$

showing that the amplitude at any point on the earth's surface, $r=a$, decreases with respect to the focal depth according to the exponential law

$$e^{-\alpha(f/a)^{\frac{1}{2}}},$$

where

$$\alpha=\sqrt{2n(n+1)}.$$

As shown by Jeans, these surface waves represent a complete system of free vibrations, and so travel round and round the globe without any loss of energy except that due to dissipative forces such as viscosity; there is no tendency for these waves to diffuse into the earth's interior. Now,

$$\alpha=\sqrt{2}\,.\,\frac{ap}{v},$$

v being the velocity of propagation of the waves considered; that is to say,

$$\alpha=\frac{2\pi a}{Tv}\,.\,\sqrt{2}=\frac{40{,}000}{20\times 4}\sqrt{2}=707 \text{ nearly},$$

taking $T=20$ seconds, $v=4$ km. per second, and $2\pi a=$circumference of the earth$=40{,}000$ km. If, then, A denotes the amplitude of the surface waves recorded at any station produced by an earthquake the focus of which is situated on the surface, then, when the focus is

(1) 10 km. deep, the amplitude $= Ae^{-28}$,
(2) 100 km. deep, the amplitude $= Ae^{-88}$,
(3) 1000 km. deep, the amplitude $= Ae^{-277}$.

This shows a more rapid diminution of amplitude of surface waves with respect to the focal depth than what was found in art. 4. When these results are used with the arguments employed in art. 6, it would appear that a depth of even 100 km. is too much for an earthquake focus.

To obtain the surface waves caused by the primary disturbance, we assume that in the neighbourhood of $r=a-f$ the solutions of the differential equations (60) and (62) in Jeans's paper are

$$w' = \mathrm{A}e^{-lr}\cos\left\{[n(n+1)]^{\frac12}\theta \pm pt\right\},$$

$$\mathrm{P}_0 = \mathrm{B}e^{-mr}\cos\left\{[n(n+1)]^{\frac12}\theta \pm pt\right\},$$

where

$$l^2 = \frac{n(n+1)}{(a-f)^2} - p^2\frac{\rho}{\mu}, \qquad m^2 = \frac{n(n+1)}{(a-f)^2} - p^2\frac{\rho}{\lambda+2\mu},$$

so that the boundary equation (65) in Jeans's paper becomes

$$lm\frac{n(n+1)}{a^2} = \left[\frac{n(n+1)}{a^2} - \tfrac12 p^2\frac{\rho}{\mu}\right]^2.$$

Squaring both sides of this equation and substituting for l^2 and m^2, we obtain

$$\left[\frac{n(n+1)}{(a-f)^2} - p^2\frac{\rho}{\mu}\right]\left[\frac{n(n+1)}{(a-f)^2} - p^2\frac{\rho}{\lambda+2\mu}\right]\frac{n^2(n+1)^2}{a^4}$$
$$= \left[\frac{n(n+1)}{a^2} - \tfrac12 p^2\frac{\rho}{\mu}\right]^4.$$

When $f=0$, this equation simplifies to

$$(\lambda+2\mu)\theta^3 - 8(\lambda+2\mu)\theta^2 + 8(3\lambda+4\mu)\theta - 16(\lambda+\mu) = 0,$$

where
$$p^2 = \frac{n(n+1)}{a^2}\cdot\frac{\mu}{\rho}\theta.$$

These surface waves then become identical with the usual Rayleigh waves. Now,

$$l^2 = \frac{n(n+1)}{a^2}\left(1+\frac{2f}{a}\right) - p^2\frac{\rho}{\mu}$$
$$= \frac{n(n+1)}{a^2}\left[1+\frac{2f}{a} - p^2\frac{\rho}{\mu}\frac{a^2}{n(n+1)}\right]$$
$$= \frac{n(n+1)}{a^2}\left[1-\theta+\frac{2f}{a}\right],$$

and

$$m^2 = \frac{n(n+1)}{a^2}\left(1+\frac{2f}{a}\right) - p^2\frac{\rho}{\lambda+2\mu}$$
$$= \frac{n(n+1)}{a^2}\left[1-\frac{8}{17}\theta+\frac{2f}{a}\right],$$

since for the earth λ/μ is probably about $1\frac18$.

For these types of waves, then, the laws of diminution of amplitude with respect to the focal depth are

$$e^{-\alpha\left(\frac{1-\theta}{2}+\frac{f}{a}\right)^{\frac{1}{2}}} \text{ and } e^{-\alpha\left(\frac{17-8\theta}{34}+\frac{f}{a}\right)^{\frac{1}{2}}}$$

for ω' and P_0 respectively, where α has the same value as before, namely

$$\alpha = \sqrt{2n(n+1)}.$$

Now $\sqrt{\theta}=0\cdot9218$ and we get therefore for these waves a slightly more rapid diminution of amplitude with respect to the focal depth than what we found in art 4.

8. *Experimental Evidence in support of "High" and "Deep" Focus.*

A method for estimating the depth of focus, based on an empirical formula for the reception of primary waves at stations near the anticentre, has been recently developed by Prof. Turner *. The method suggests a normal depth *d* for the focus, which has some such value as 0·04 of the earth's radius. Several earthquakes have been studied by Turner by this method, and focal depths both above and below the normal depth have been assigned to them. There is some uncertainty about the value of *d*, but the following cases of "high" focus will not be inconsistent with the results obtained in this paper :—

Year.		Date. d	h	m	s	Epicentre.		Focal Depth.
1918	Sept.	7	17	15	51	46°·5 N.,	151°·4 E.	$d-{\cdot}030$
„	„	8	0	9	30	„	„	$d-{\cdot}030$
„	„	11	4	6	5	„	„	$d-{\cdot}030$
1919	May	6	19	40	45	6°·0 S.,	153°·0 E.	$d-{\cdot}030$

The values obtained for the depths of the "deep" focus are inappropriate with the conclusions of this paper.

Dr. Dorothy Wrinch, by an altogether different procedure, finds that the observations of the Calabrian earthquake of 1905, September 8, taken at stations at distances of between 40 and 220 km., give 40 to 50 km. as an upper estimate of the depth of its focus, in agreement with the results obtained in this paper. It will perhaps be better to postpone criticism of the experimental results so far obtained till a method has been determined for finding out the actual depth instead of the relative depth of the focus from the observed data ; but the suggestion may be put forward that the systematic deviation from the time of arrival of the first waves as given by the empirical formula of Turner, which any particular earthquake is liable to show at all antipodal stations, may to a certain extent be due to the effect of the rotation of the earth which the formula does not take account of. The effect will be negative or positive, according as the wave systems travel in or against the direction of rotation of the earth. It is proposed to discuss this effect in a subsequent paper.

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* 'Monthly Notices of the Royal Astronomical Society,' Geographical Supplement, vol. i. no. 1 (1922).

9. *Summary and Conclusion.*

The conclusions of this paper may be summarized as follows. When the earth is assumed to be an infinite solid bounded by a plane, it is found that—

(1) The amplitudes of the long wave phase in the seismogram undergo a very rapid diminution with increasing depth of focus. If f = the depth of focus, the amplitude is proportional to $e^{-\alpha_1 f}$, and when f is expressed in kilometres, the value of α_1, under typical conditions, is $\frac{1}{10}$.

(2) The effect of the depth of the focus on the amplitudes of the P and S waves at large epicentral distances is almost negligible.

(3) If the depth of the focus is 1000 km., then the seismogram at a station very near the anticentre should show the amplitude of the P and S waves about $2{\cdot}7 \times 10^{37}$ times larger than the amplitude of the L waves, assuming that all these waves had the same amplitude at unit distance from the source. This is contrary to facts, and therefore a depth of 1000 km. is too large an estimate for the depth of earthquake focus.

(4) If the depth is 200 km., then the amplitude of P and S phases at the same station would be 400 times larger than the amplitude of the L phase. The earthquake focus is therefore probably not even 200 km. deep.

(5) If the depth is 100 km., then the amplitude of the L waves is about 55 times larger than the amplitude of the P or S waves. Roughly speaking, therefore, 100 km. or anything in the neighbourhood of 100 km. or less than 100 km. is a possible depth for the earthquake focus.

When the earth is assumed to be a perfectly spherical body, it is found that the effect of the focal depth on the amplitude of the Rayleigh waves becomes more accentuated, and the results indicate that the depth is probably less than 100 km.

My best thanks are due to Sir Gilbert T. Walker, F.R.S., for the interest he has taken in the paper.

The Observatory,
Colaba, Bombay,
July 7, 1924.

VII. *Turbulence and Vertical Temperature Difference near Trees.* *By* LEWIS F. RICHARDSON, *B.A.*, *F.Inst.P.*[*]

CONTENTS.

§ 1. Introduction.
§ 2. The Vertical Difference of Temperature.
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§ 6. Personal.
§ 7. Summary.

§ 1. *Introduction.*

WHEREAS Osborne Reynolds's criterion of turbulence agrees fairly well with the behaviour of the fluid in a pipe, yet in the open air it is known that the up-gradient of temperature exerts in addition a strong controlling influence. This problem is explored by observations, which are brought into relation with a theory already published.

§ 2. *The Vertical Difference of Temperature.*

In order to measure the temperature-difference, a thermo-electric arrangement was set up (as shown in fig. 1) partly on an iron mast, partly on a tree. The junctions α and β were 4·4 and 18·3 metres above the ground. Radiation and rain were screened off by horizontal zinc plates, two above and one below each junction. The uppermost plate was about 30 cm. in diameter. This type of screen was a modification of one devised by the Indian Survey Department. A thick eureka wire passed directly from one screen to the other, and from its ends copper wires were led to a very sensitive moving coil galvanometer of 1·9 ohms resistance by Hartmann & Braun.

The arrangement was standardized by preparing two vacuum jacketed flasks containing paraffin oil at slightly different temperatures. One junction was placed in each flask, the galvanometer was read, the flasks interchanged, and the reading repeated. The temperature difference of the oil was taken before and after by mercury thermometers. Five comparisons were also made with an aspirated thermometer carried up and down the mast. These readings confirmed in a rough way the standardization by oil, but, as they were not simultaneous at top and bottom, they are considered to be less accurate. The galvanometer could be read to 0°·003 C., and was certainly reliable to 0°·03 C.

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[*] Communicated by the Author. Read at the British Association for the Advancement of Science, Toronto, 1924.

Care was taken not to record any observation when either junction was likely to be wet by rain, nor when horizontal sunbeams fell on it.

Fig. 1.

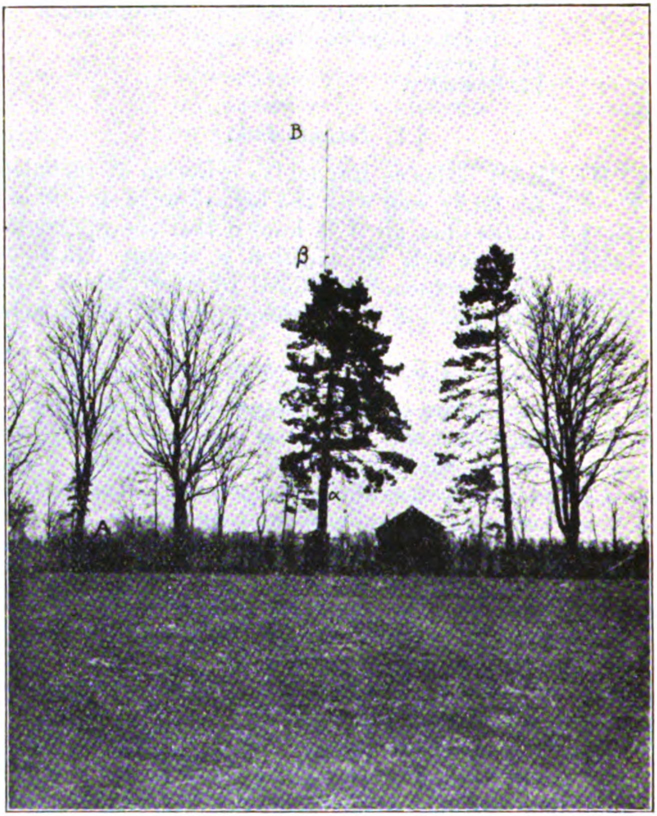
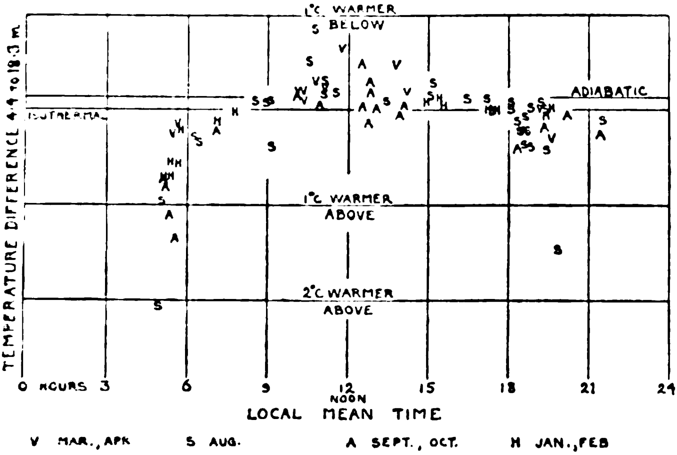


Fig. 2 shows the diurnal variation of the difference of temperature. If the zinc radiation-screens were inadequate, then the upper junction would on the average be warmest, relatively to the lower junction, at mid-day when sun could shine directly on the zinc plates of the upper junction, while the lower junction was under the shade of a fir-tree. Actually the reverse is observed, hyper-adiabatic gradients being frequent between 10 h. and 16 h. G.M.T. These facts lead me to believe: firstly, that the screening was efficient; and secondly, that hyper-adiabatic gradients did really exist. At the times when such gradients were recorded the galvanometer oscillated irregularly, as we should expect if, owing to the instability, the warm air was rising in streaks and patches.

Fig. 2.



§ 3. *The Mean Wind and the Gusts.*

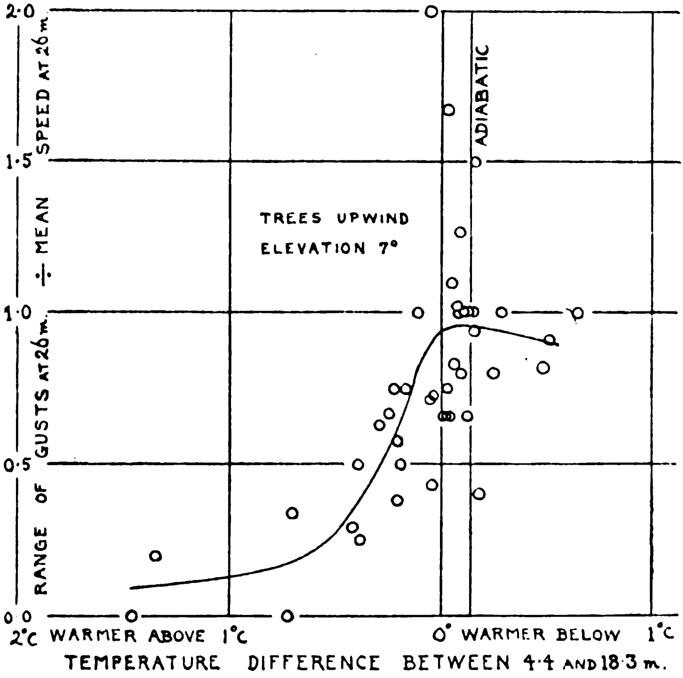
The wind velocity and direction were measured by a Dines anemometer at a height of 26 m. above the ground, and at a height of 2 m. by a small windmill anemometer also of Mr. W. H. Dines' design.

The turbulence at 26 m. was indicated by the range of gusts shown on the trace of the P.T. anemometer. By gusts are meant those variations of wind which cause the anemometer pen to go to and fro many times within an interval of ten minutes. The slower variations having periods lying between say 10 minutes and an hour are not discussed here. It being common knowledge among meteorologists that the range of gusts is, on the average, proportional to the mean velocity at the same level, the ratio of the former to the latter has been given the name "gustiness," and has been a subject of various studies.

Fig. 3 exhibits the gustiness at 26 m. as a function of the difference of temperature in a layer below that level. In spite of the considerable scatter, which may be due to the different exposures in directions here lumped together, it is evident that the gustiness varies on the average somewhat in the way indicated by the line drawn on the diagram. As we should expect, the gustiness is small when the air is much colder below, and increases as the labile adiabatic equilibrium is approached. It is surprising, however, to observe that, as far as the scanty observations go, the unstable hyperadiabatic condition did not correspond to still further increased gustiness.

An analogous peculiarity has been noted in the upper air, as may be seen from the dotted line in the diagram on p. 78 of "Weather Prediction by Numerical Process"*.

Fig. 3.



Let us now consider winds from directions in which the trees were much further away, subtending an elevation of only 1° at the instruments instead of 7°. It was found that for adiabatic conditions:—

Mean wind at 26 m.	7·5 m/s.	4 m/s.
Range of gusts at 26 m.	5 m/s.	2·5 m/s.
Gustiness $= \dfrac{\text{range of gusts}}{\text{mean wind}}$ ...	0·67	0·62

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* Cambridge University Press.

It is seen that on fig. 3 the corresponding ratio is 0·95 when the trees subtend 7°.

§ 4. *The Theoretical Criterion of Just-no-turbulence.*

Another way of regarding the turbulence, a way which is less simple but more likely to give us insight into the processes at work, will be to bring the observations into relation with a certain "criterion" deduced from theory, in a paper* on the Supply of Energy from and to Atmospheric Eddies. It may help to clear ideas if I repeat in a simple form the fundamental notions of the previous paper, especially as it dealt with the whole thickness of the atmosphere, whereas our present observations are in a layer comparatively thin.

Imagine a horizontal slab of air bounded by fixed pressures $p+\delta p$ and p. Its mass per area is $\delta p/g$, and remains fixed as it is warmed. If θ denotes its absolute temperature and γ_v denotes the specific heat of air at constant volume, then the rate at which the slab acquires thermal energy is denoted by $(\delta p/g)\gamma_v . \partial\theta/\partial t$, where t is the time. We shall suppose that specific heats are expressed with ergs not calories. As the slab is warmed, it swells, lifting the air above, which therefore acquires gravitational energy. It may be shown that the rate of increase of this gravitational energy is $(\delta p/g) . b\partial\theta/\partial t$, where b is the gas-constant in $p=b\rho\theta$. This is also evident because $\gamma_v+b=\gamma_p$, the specific heat at constant pressure, and because we can include both effects by simply thinking of the air as being warmed at constant pressure. If the material of the slab were a solid such as copper or marble, then, as Fourier stated, the excess of the heat flowing in at one face over the heat flowing out at the other just accounts for the rate of increase of the heat contained in the slab. No heat appears or disappears. But if the slab is air and the flux of heat is due to eddy-conductivity, then the excess of the flux into, over the flux out of, the slab does not in general equal the rate of gain of thermal energy in the slab. There is an extra part, which may be of either sign, and which is presumably a rate of gain or loss of energy of the eddies. To put these things in the notation of the former paper we have the diffusion equation

$$\frac{\partial\theta}{\partial t}=\left(\frac{p}{p_i}\right)^{0\cdot29}\frac{\partial}{\partial p}\left(\xi\frac{\partial\Phi}{\partial p}\right),$$

where θ is absolute temperature, Φ potential temperature, namely the temperature which the air would attain if brought adiabatically to a standard pressure p_i, and ξ is the turbulivity.

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* L. F. Richardson, London Roy. Soc. Proc. A, vol xcvii. p. 354 (1920).

Instead of making a partial integration, as formerly, let us apply the formula for the differentiation of a product to the second member. Then after multiplying by $\gamma_p . \delta p/g$ we have

$$\gamma_v \frac{\delta p}{g} \frac{\partial \theta}{\partial t} + b \frac{\delta p}{g} \frac{\partial \theta}{\partial t} = \gamma_p \frac{\delta p}{g} \frac{\partial}{\partial p} \left\{ \left(\frac{p}{p_i} \right)^{0 \cdot 29} \xi \frac{\partial \Phi}{\partial p} \right\}$$

$$- \frac{\gamma_p \delta p}{g} \frac{\partial \Phi}{\partial p} \frac{0 \cdot 29}{p_i} p^{-0 \cdot 71} .$$

The first term in this equation is the rate of increase of thermal energy inside the slab, the second term is the associated rate of increase of gravitational energy in the whole of the atmosphere above the slab. In the second member the first term has been shown elsewhere to be the difference between the fluxes of heat over the two faces of the slab. Consequently the last term must be the rate, per area and per time, of a supply of energy to the eddies. After various uninteresting transformations it is shown that this supply to the eddies amounts per volume to

$$\frac{cg}{\theta} \left\{ \frac{\partial \theta}{\partial h} - \frac{\partial \theta_A}{\partial h} \right\} = \left(\frac{\partial e'}{\partial t} \right)_1 \text{ say,}$$

where $\partial \theta_A / \partial h$ is the adiabatic up-gradient of temperature and c is the "eddy-conductivity" defined by

$$\frac{\bar{D} \Phi}{\bar{D} t} = \frac{1}{\rho} \frac{\partial}{\partial h} \left(c \frac{\partial \Phi}{\partial h} \right),$$

where ρ is the density and $\bar{D}$ a differentiator following the *mean* motion.

The other causes of supply of energy to and from eddies must now be named. As Osborne Reynolds showed, eddy energy is produced by shearing of the mean-wind at a rate per volume equal to

$$\left(\frac{\partial e'}{\partial t} \right)_2 = \mu_{XH} \left(\frac{\partial \bar{v}_X}{\partial h} \right)^2 + \mu_{YH} \left(\frac{\partial \bar{v}_Y}{\partial h} \right)^2 ,$$

where μ_{XH}, μ_{YH} are eddy-viscosities.

Next it is obvious that molecular viscosity μ_e damps out eddies. In the former paper it is shown that in some instances, taken as typical, $(\partial e'/\partial t)_3 = -\frac{2\mu_c\pi^2}{\rho l^2}e'$, where l is a conventional linear dimension of an eddy and ρ is the air-density.

Lastly it seems likely that eddy-energy, produced in a thin layer, surrounded by non-turbulent air, will not all remain in the layer, but that some of it will disperse as eddy energy. A rough experiment to illustrate this effect was made in a domestic bath full of still water. A fountain pen-filler, 1·1 cm. in diameter, was drawn in a straight line through the top of the water at a speed of 31 cm. sec.$^{-1}$ and was squeezed meanwhile so as to leave a wake of inky eddies. These gradually spread out into the still water. The extreme width s of the ink-trail was observed in the middle of the bath every 20 seconds. It was found that $s^{2\cdot4}$ was proportional to t the time from the formation of the trail. The standard deviation of the ink from the middle of the lamina must have been of the order of $s/3$, so that, if we had to do with the spreading of a lamina in a medium of uniform diffusivity, and this is a very rash hypothesis, s^2 would be proportional to t, and the diffusivity would be of the order of $(s/3)^2/2t$. In the present instance this diffusivity came very roughly to $\frac{1}{3}$ cm.^{2}sec.$^{-1}$. Such a diffusivity, if it exists, probably increases both with the size of eddies and with the speed of their particles. All we can do at present in connexion with turbulence among trees is to neglect this effect, and to notice whether we are thereby led to false conclusions. As a reminder of its existence let us denote this part of the rate of supply per volume of energy to eddies by $(\partial e'/\partial t)_4$.

Collecting terms

$$\frac{\partial e'}{\partial t} = \left(\frac{\partial e'}{\partial t}\right) + \left(\frac{\partial e'}{\partial t}\right)_2 + \left(\frac{\partial e'}{\partial t}\right)_3 + \left(\frac{\partial e'}{\partial t}\right)_4$$

$$= \frac{cg}{\theta}\left\{\frac{\partial\theta}{\partial h} - \frac{\partial\theta_A}{\partial h}\right\} + \mu_{XH}\left(\frac{\partial v_X}{\partial h}\right)^2 + \mu_{YH}\left(\frac{\partial v_Y}{\partial h}\right)^2$$

$$- \frac{2\mu_c\pi^2}{\rho l^2}e' + \left(\frac{\partial e'}{\partial t}\right)_4. \quad . \quad (1)$$

G. I. Taylor * and Schmidt † have given reasons for believing that $c = \mu_{XH} = \mu_{YH}$. If we neglect the dispersal of eddies, then as the term $-2\mu_c\pi^2 e'/(\rho l^2)$ due to molecular

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* G. I. Taylor, "Eddy Motion in the Atmosphere," Phil. Trans. Roy. Soc. A. ccxv. (1914).

† Schmidt, *Akad. Wiss. Wien*, 1917.

viscosity tends to make $\partial e'/\partial t$ negative until e' vanishes, it follows that eddies will just die away if

$$\left(\frac{\partial v_X}{\partial h}\right)^2 + \left(\frac{\partial v_Y}{\partial h}\right)^2 = \frac{g}{\theta}\left\{\frac{\partial \theta}{\partial h} - \frac{\partial \theta_A}{\partial h}\right\} \quad . \quad . \quad . \quad (2)$$

C. K. M. Douglas * has recently shown that this criterion (2) will explain the scarcity of sudden inversions of temperature in the upper-air.

When we compare formula (2) with observation we have to replace infinitesimals by finite differences, and it must be admitted that the differences of 14 and 24 metres which have been employed are rather too large for this region of steep non-linear gradients; and further that it would have been better, had it been possible, to have made the two ranges coincident, to have measured the turbulence in the middle instead of at the top, to have recorded the direction of the lower as well as of the upper wind, and to have had the trees quite uniform in size, kind, and arrangement. However, in spite of all these imperfections, we shall find something of interest.

If v_{26} and v_2 are the wind speeds in metres per second at 26 and 2 metres above ground, and if the junction at 18·3 metres is t°C. warmer than the junction at 4·4 metres, then formula (2) takes the approximate form

$$(v_{26} - v_2)^2 = 1{\cdot}43(t + 0{\cdot}137) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The approximation consists in neglecting the variation of wind direction between the two levels. I doubt if it ever exceeded 20° and consequently it was not important.

To compare the observations with formula (3) a diagram (fig. 4) has been constructed having vertical temperature-difference for one coordinate and vertical wind-difference for the other. Each observation is represented by a point on the diagram, and the range of gusts on that occasion is written on the diagram as a number having its centre at the point in question. The curve represented by equation (3) is plotted on the diagram, and it is found that it does really lie near the boundary of the region of no gusts. This is surprising when we consider that among trees the mean wind does not flow in straight lines but bends round every leaf and twig, so that we might reasonably expect that friction with the trees would generate eddy-energy at a considerable rate, in addition to the part represented by the first member of (2). The present observations therefore

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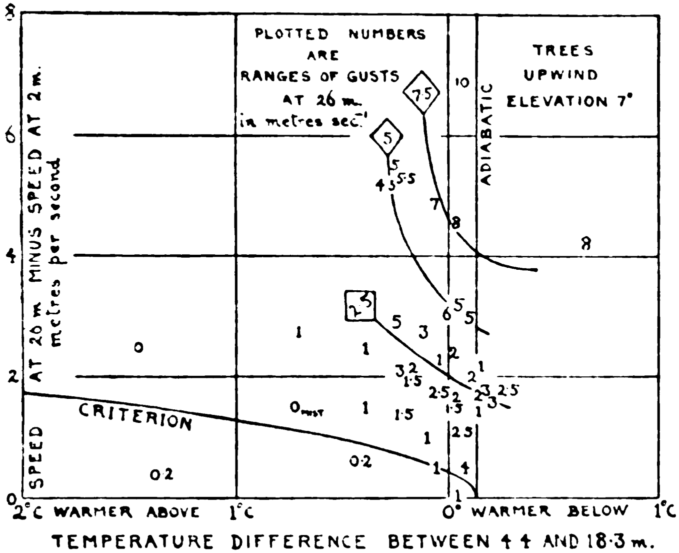
* Quart. Journ. Roy. Meteor. Soc. Oct. 1924, p. 359.

suggest that the two members of equation (2) are derived from the most important parts of the rate of generation of eddy-energy, even when there are trees close below the level where the turbulence is measured.

Fig. 4.



§ 5. *Degrees of Turbulence.*

Most of the observations lie far away from the criterion in the gusty region. Isopleths of range of gusts have been sketched to represent the observations. In this region the eddy-energy would be increasing if the second member of (2) represented the only cause acting to decrease it There is of course another cause; the breaking up of large eddies into smaller ones which in turn are damped out by molecular viscosity. Apparently this cause is important when turbulence is great and yet negligible near the criterion.

§ 6. *Personal.*

These observations at Benson Observatory (Long. 1° 6′ W., Lat. 51° 37′ N.) were begun as an official duty on the field of Mr. W. H. Dines, by whom they were helped on. The screens were made by Mr. B. C. Lewis. The results are communicated by permission of the Director of the Meteorological Office.

§ 7. *Summary.*

(1) Statically unstable vertical gradients of temperature were common between heights of 4·4 m. and 18·3 m. in the middle of the day. See fig. 2.

(2) The "gustiness" at 26 m. increased as the layer below became less statically stable. But after the layer had passed the labile adiabatic condition, the gustiness did not further increase, although the layer below was definitely unstable. See fig. 3.

(3) The criterion of just-no-turbulence, published by the author in 1920 *, is in rough agreement with the observed facts; in spite of the friction of the air on the trees. See fig. 4. But the observations do not give a definite answer to the question as to whether a factor of 2 does come in, as it would according to calculations by G. I. Taylor if the eddies developed from waves in shearing laminæ.

(4) Isopleths of the range of gusts are drawn on fig. 4 for the region far from the criterion.

VIII. *Periodic Precipitation in Dilute Gelatine Gels.*

By G. W. SCOTT BLAIR, *B.A.*, *Trinity College, Oxford* †.

[Plate III.]

WHEN the solution of one salt is allowed to diffuse into a jelly containing another salt with which the first interacts to give a sparingly soluble compound, the precipitate is formed in many cases in separate rings instead of in a continuous band.

This phenomenon, which was discovered by Liesegang, has been shown to be the cause of many periodic formations in nature, and is thus of considerable importance.

The effect of the conditions of the gel on the phenomenon.—The experiments of Dreaper (*Koll. Zeitschr.* xiv. p. 163, 1914), Kauer (J. A. C. S. xliv. p. 951, 1922), and Chapin (see Holmes, J. A. C. S. xl. p. 1189, 1918) have shown that the phenomenon can take place in the absence of gels ; but there can be no doubt that the nature and concentration of the gelatine exert a profound influence. [See Liesegang, *Koll. Zeitschr.* ii. p. 73 ; Hausmann, *Zeit. für Anorg. Chem.* xl. p. 110, 1904 ; Köhler, *Koll. Zeitschr.* xix. p. 65, 1916 ; Bradford, Biochem. Journ. x. p. 169, 1916, etc.]

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* Roy. Soc. Proc. A. xcvii. p. 354 (1920).

† Communicated by the Author.

Liesegang points out in the paper quoted above that the age of the gel may modify ring formation, but he does not arrive at any very definite conclusions on the subject.

It seemed that further work should be carried out on the effect of the age of the gel on the formation of rings. Experiments described in this paper and illustrated in Pl. III. show the rather remarkable effect of age. In these experiments silver nitrate diffused into potassium bichromate in dilute gelatine. The gels were made up under standard conditions—10 per cent. silver nitrate, 0·019 per cent. potassium bichromate, and 0·5 per cent. and later 1 per cent. gelatine being used. It will be seen that in a given tube in which ring formation occurs the number of rings formed is quite definite, and the distance from the surface of the last ring to be formed is quite sharp. This distance is called "a_∞." It will also be seen that a_∞ increases regularly with the age of the gel from zero-age to about ten days. With gels older than this, ring formation ceases to take place at all (traces of irregular vertical striations are, however, produced in the tube instead of regular horizontal bands). Then, with gels of very much greater age, the power of ring formation is found to be recovered once more (not shown in figure). The "*Ageing series*" exhibited by gels of age varying from 0 to 10 days is clearly shown in the figure.

A similar progressive increase of a_∞ was not found with other salt pairs; but with silver nitrate and potassium chromate, the second part of the phenomenon (failure to produce rings after a certain limit of age) made its appearance. In the case of the bichromate, this age-limit was found to increase on increasing the gelatine concentration (see Table I.).

Special experiments were made to show that the effect of ageing was not due to any of the following causes :—

(1) Changes in the rate of diffusion of the ions through the gelatine, since not only did the electrical conductivity remain unchanged as the gel aged, but also the observed rate of diffusion of various coloured salts and dyes through the gelatine was found to be independent of its age.

(2) Changes in the H-ion concentration of the system.

(3) Changes in bichromate concentration due to chemical interaction with the gelatine.

Some change in the structure of the gel is therefore indicated as the cause.

Table I.

Effect of gelatine concentration on age-limits for ring formation.

Percentage Gelatine.	Age-limit to ring formation.
0·5	6–13 days.
1	23–28 hrs.
2	10–46 hrs.
5	10–23 hrs.

Note.—Throughout the course of these experiments, the room-temperature at which they were carried out varied over about three or four degrees.

The effect of light on the phenomenon.—That light has a profound influence on the phenomenon has been shown by Davies (J. A. C. S. 1923, p. 2261), Kuester (*Koll. Zeitschr.* xiii. p. 192), Hatschek (Proc. Roy. Soc. 1921, p. 496), and Sen & Dhar (*Koll. Zeitschr.* xxxiv. p. 270, 1924). The first of these authors found that blue light was more effective than red in its action in the case of the reduction of gold chloride in silicic acid gels in which coloured bands are produced. The second found that ring formation became impossible in complete absence of light (though, since he used gels of varying ages, any generalization of his results seems impossible); and the third that in a few special cases abnormal ring formation takes place under the influence of light. The work of Sen & Dhar extends and verifies that of the above-mentioned workers.

Work has been done by the author on the effect of light of different wave-lengths on the production of silver-bichromate rings in gelatine, and it has been shown that:—

(1) Either intense white light (½ watt lamp 6 in. range) or complete darkness cause irregular ring formation, and a decrease in the value of a_x.

(2) The diminution of a_x is greater in the case of blue light than in the case of red light of the same intensity.

(3) The action of any kind of visible light is irreversible, in the sense that, after reliquefaction and resetting of the gelatine, the anomalous formation persists.

(4) Ultra-violet light from a mercury-vapour quartz lamp makes the formation of rings in a gel exposed to it for even a few hours quite impossible.

(5) Unlike the effect of visible light, which is permanent,

that of ultra-violet light does not persist if the gel is reliquefied and reset. This remarkable difference seems to be fundamental.

If the gel is exposed to the action of both types of light simultaneously, reliquefaction and resetting reverses the action of the ultra-violet but not of the visible light. Ring formation is then exactly as if the gel had been exposed to visible light only. These curious phenomena were observed repeatedly, and not merely on a single occasion.

Incidentally it may be remarked that the action of ultra-violet light does not alter the rate of setting of the gelatine.

The cause of the phenomenon.—It is clear from the above that outside factors, such as the physical conditions of the gel and the action of light, have a profound effect on the phenomenon; but, as pointed out already, the periodic nature of the precipitation is not itself essentially dependent on the presence of the gel.

The only theory as yet put forward in the literature to explain rhythmic banding which seems to be supported by strong positive evidence [see Morce & Pierce (*Zeit. für Phys. Chem.* xlv. p. 589, 1903), Jablczynski (*Bull. Soc. Chim.* 1923, p. 1594, etc.)] is that of Ostwald, who postulates that the resultant salt is retained in supersaturated solution until a sharp limit of concentration (the metastable limit) is reached, after which a precipitate is formed. Back-diffusion then impoverishes the zone immediately below the precipitate to such an extent that the metastable limit is no longer exceeded, and a clear space ensues. This process is repeated.

Although Ostwald's theory is undoubtedly the correct explanation of the phenomenon in its essentials, it requires considerable modification in detail. Three serious objections to it, as it stands, arise:—

(1) Hatschek (*Koll. Zeitschr.* x. p. 124, 1912) has found that previous sowing of the gel with nuclei of the precipitate does not relieve supersaturation, but that ring formation still takes place. The experiments, which were repeated by the author, consisted in adding a little lead nitrate to an agar sol containing potassium iodide before the sol set, so that on setting, the gel was filled with small particles of lead iodide. On allowing a solution of lead nitrate to diffuse into this gel, rings were formed quite independently of the presence of the lead-iodide nuclei throughout the gel.

(2) The fact that the condition of the gel has a profound effect on ring formation is quite unexplained.

(3) On the simple Ostwald theory, the values of $a/\sqrt{t}$

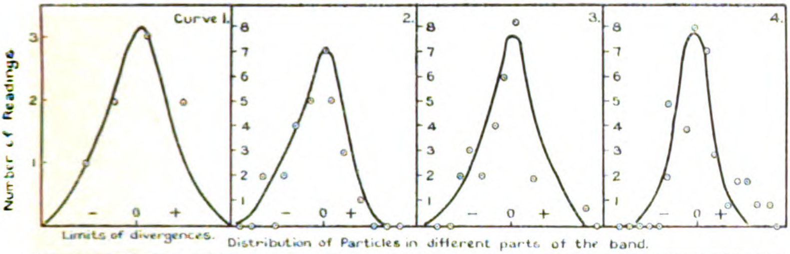
(where a is the distance of any ring from the origin, and t is the time interval from the addition of silver nitrate to the tube until the ring is formed) should be constant. Morse & Pierce found that this was approximately the case (*loc. cit.*); but the author, by observing carefully the exact time of formation of the rings, has shown that the values fluctuate about a mean constant value to a degree unexplainable on the hypothesis of mere errors in measurement (see p. 96).

The following modification of Ostwald's theory, which seems to avoid these three difficulties, has been suggested to me by Mr. C. N. Hinshelwood. There is no absolutely sharp metastable limit, but only a region of concentration where precipitation becomes very probable. In the immediate neighbourhood of the ordinary solubility limit precipitation is very unlikely, in the sense that it would only occur on the average after a very long time. This probability of crystallization increases very rapidly when we get to a certain region of concentration, but there is no sharp limit above which precipitation does occur and below which it does not occur (*cf.* Hinshelwood & Hartley, Phil. Mag. xliii. p. 78, 1922). The second suggestion is that the micelles of the gel itself may act as crystallizing centres for the formation of precipitate, just as colloidal particles of the right size were found to provoke the crystallization of supercooled liquids in the paper referred to.

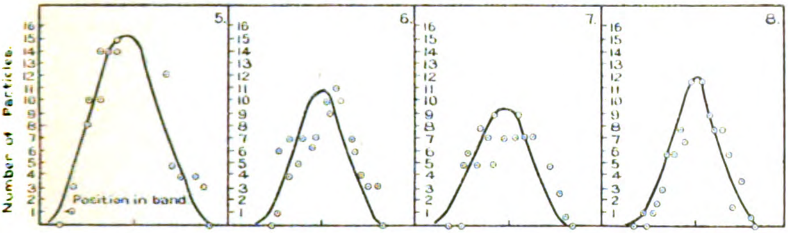
The first part of this suggestion has been tested by the author in two ways, and in both cases the evidence obtained seemed strongly to favour the above explanation. In the first place, as mentioned above, the exact times of precipitation of rings in about 8 tubes simultaneously were noted, and values of $a/\sqrt{t}$ were worked out. The curves obtained by plotting the number of values of $a/\sqrt{t}$ within various fixed distances from the mean value are given, and give a curve of the usual probability type (see curves 1–4). It can be easily shown from known errors in a that the discrepancies in $a/\sqrt{t}$ are far too great to be due merely to experimental error in measurements of a and t (see p. 96).

In the second place, the idea of a metastable region as above described should manifest itself in a falling off of the number of particles in the rings from the centre in accordance with the ordinary chance distribution. Certain plates of Hatschek and Liesegang seem to show such a falling off (*e.g.* Soc. of Chem. Ind. Proc. xxx. p. 256, 1911), though neither author comments on it; but it has been found possible in this work to get much more definite information on this score by producing rings so wide, and containing so few particles of precipitate, that the number in different parts of the ring could be counted under a high-power microscope. The resulting curves (curves 5–8) are of a form in complete accordance with the probability theory. It is not surprising, on this theory, that the conditions of the gel should affect ring formation. Whether we consider the formation of a visible precipitate as spontaneous crystallization, or as the coagulation of already formed colloidal silver bichromate, is immaterial. In the former case it is possible, as stated above, that the micelles of the gelatine act as crystallizing nuclei when of the appropriate size and when the appropriate concentration is reached: the variation of effectiveness with age depends on the supply of micelles of appropriate size, since ageing is known to increase the size of the micelles. (This increases a_∞, whereas the action of light, which is shown to diminish the micellar size, diminishes the value of a_∞.) If we take the second view, the condition of the gelatine would certainly influence the phenomenon profoundly, in so far as it would exert a greater or less protective effect on the coalescing particles. But further, the idea that the micelles of the gel of appropriate size are themselves crystallizing centres, avoids the difficulty of the inoculation experiments.

Distribution of Values of $a/\sqrt{t}$



Distribution of Particles in different parts of the band.



Proof that the discrepancies in values of $a/\sqrt{t}$ are not due to reading errors :—

Data :

Measurements gave the following :—

Mean value of $a/\sqrt{t}$ for all readings	(y)	0·00908	c.g.s. units.
Mean value of a ,, ,,	(a)	0·4897	
Mean value of t ,, ,,	(t)	3063	
Mean error in reading a (determined)	(Δa) ...	0·011	
Mean discrepancy in $a/\sqrt{t}$	(Δy) ...	0·00049	

From these figures we can calculate what the error in reading t should be, if we assume that the discrepancies in $a/\sqrt{t}$ are due entirely to errors in reading.

From the equation

$$\log y = \log a - \tfrac{1}{2} \log t$$

we get

$$1/y \, . \, \Delta y = 1/a \, . \, \Delta a - 1/2t \, . \, \Delta t,$$

or

$$\Delta t = 2t(\Delta a/a - \Delta y/y).$$

Assuming the errors in a and y to be

(1) Of the same sign :	(2) Of opposite sign :
$t = 6126(0{\cdot}0011/0{\cdot}4897$ $+0{\cdot}00049/9{\cdot}00908)$	$t = 6126(0{\cdot}0011/0{\cdot}4897$ $-0{\cdot}00049/0{\cdot}00908)$
$= 6126 \times 0{\cdot}05621$	$= 6126 \times 0{\cdot}05171$
= 5 min. 44 sec.	= 5 min. 17 sec.

In either case this is absurd as a mean error in reading t, which can be read easily to the nearest second at the outside, so that the original assumption is unjustified, and we are brought to the conclusion that the discrepancies in $a/\sqrt{t}$ are not due merely to errors in reading a and t.

Conclusions.

It is shown in this paper that the age of gels profoundly influences Liesegang ring formation in them.

The effect of light of various wave-lengths has been investigated. A fundamental difference between the effects of ultra-violet light and of visible light has been found.

A new modification of the Ostwald theory of the phenomenon is discussed, and evidence in its favour put forward.

In conclusion, I should like to express my gratitude to Mr. C. N. Hinshelwood, who has directed this research throughout, and whose suggestions and criticisms have made possible the production of this paper.

Trinity College, Oxford,
July 18th, 1924.

IX. *On the Forces at the Ends of a Vibrating String.* By W. H. GEORGE, *M.Sc., University College, Nottingham* *.

Summary.—The paper deals with the magnitude and frequency of those forces at the ends of a vibrating string which are due to the tension of the string. The influence upon the length of the string of its change of shape when vibrating is calculated, and the result is used to determine the increase in tension. Incidentally, the maximum tension for a given amplitude of vibration is determined theoretically, and numerical values are calculated and compared with the tensions used for pianoforte strings where high tensions are shown to be of great importance. The effect of the inclination of the vibrating string upon the longitudinal and normal forces at the ends of the string is illustrated graphically. Calculations of the resultant longitudinal and normal components for two steel wires of different diameter are given and show the importance of the longitudinal component which is of double frequency. Experimental work by Barton, Raman, Berry, and others dealing with actual bridges and showing the presence of the double frequency vibrations in the longitudinal motions of the bridges, is quoted. Finally, an anomalous excitation of the nth partial by striking a string at $1/n$th of its length from the nearer bridge is discussed.

IN treating of the theory of the transverse vibrations of strings, the string is usually taken to be a perfectly uniform and flexible filament of solid matter stretched between two fixed points, and the tension is assumed to be constant throughout the motion. The string used in experimental acoustics approximates closely to this ideal, and the small deviations from the ideal have been studied theoretically and experimentally by various workers. It would appear, however, that the yielding of the supports is of special importance and is worthy of still further study. It is well known that the aerial vibrations directly set up by a vibrating string are almost if not quite inaudible, and that the audible vibrations are generated by the motion of the larger surfaces to which the ends of the string are attached. If, then, these ends were fixed, the vibrating string would be inaudible. Motion of an end of the string is also tacitly assumed when the tuning of the string is tested by pressing the stem of a vibrating tuning-fork upon one of the ends.

Rayleigh [‘Sound’, i., § 135] has considered in what manner the vibrations of a string are liable to be modified by a yielding of the points of attachment. Assuming the system frictionless and symmetrical with reference to the centre of the string, he finds (i.) that if each end be attached to a particle of mass (M) there is a rise in pitch, the rise being greater the lower the component tone, and (ii.) that if each end is urged by a spring (μ) towards the position of equilibrium then the pitch of the whole series of partials is slightly lowered. In an actual case, where both mass and spring factors are present, the raising or lowering of pitch will depend on whether the natural note of the mass (M), urged by the spring (μ), is lower or higher than that of the component vibration in question. Experimental work bearing on the motion of the ends will be referred to later, and we will now consider the forces which cause this motion. We have (i.) the change in length and consequent change in tension of the string due to its change of shape, and (ii.) the change in direction at the ends of the string of the force due to its tension.

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* Communicated by Prof. E. H. Barton, F.R.S.

EXTENSION OF THE VIBRATING STRING.

Since the increase of tension can be calculated from the increase in length, we will first calculate the increase in length of the string due to its varying shape. The shape of the string at any instant t is given by the equation

$$y = \sum_{s=1}^{s=\infty} \sin\frac{s\pi x}{l_0}\left(\mathrm{A}_s\cos\frac{s\pi at}{l_0} + \mathrm{B}_s\sin\frac{s\pi at}{l_0}\right), \quad . \quad (1)$$

giving the displacement y of any point x, the origin of coordinates being at one end of the string, which is here assumed to be perfectly uniform and flexible, to be held fast at both its ends distant l_0 apart, and to vibrate under uniform tension in one plane only. The notation is otherwise as in Rayleigh's 'Sound,' i. § 124. Since the length (l) of the string is given by

$$l = \int_0^{l_0} \sqrt{1+(dy/dx)^2}\,.\,dx,$$

we have:

$$l = \int_0^{l_0}\left[1 + \sum_{s=1}^{s=\infty}\frac{s^2\pi^2}{l_0^2}\cos^2\frac{s\pi x}{l_0}\left(\mathrm{A}_s\cos\frac{s\pi at}{l_0} + \mathrm{B}_s\sin\frac{s\pi at}{l_0}\right)^2\right]^{\frac{1}{2}}.\,dx.$$

$$. \quad . \quad . \quad (2)$$

String Sounding Fundamental.—To calculate the order of magnitude of the extension we must take some special case, since the values of the coefficients A_s and B_s depend on the initial values of (y) and (dy/dt). The simplest case, from which all others can be deduced, is that of the string sounding its fundamental only. If the maximum displacement of the middle point of the string be A, then equation (1) reduces to

$$y = A\sin\frac{\pi x}{l_0}, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1\,a)$$

and

$$l = \int_0^{l_0}\sqrt{1+\frac{A^2\pi^2}{l_0^2}\cos^2\frac{\pi x}{l_0}}\,.\,dx.$$

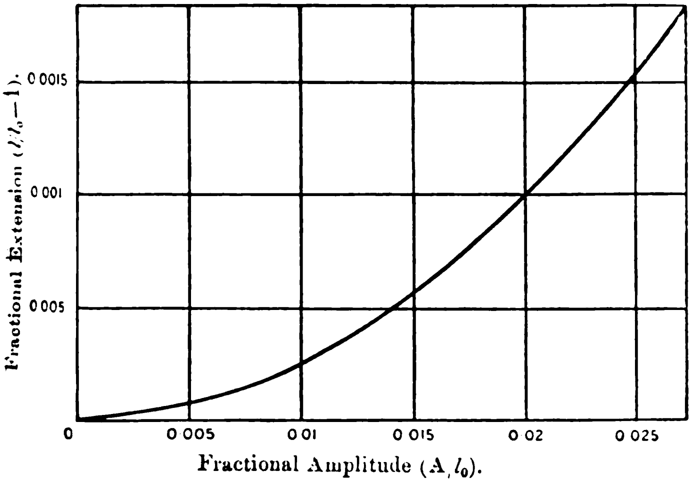
This can be rewritten:

$$l = \sqrt{1+K^2}\int_0^{l_0}\sqrt{1-\frac{K^2}{1+K^2}\sin^2\frac{\pi x}{l_0}}\,.\,dx,$$

where $K = A\pi/l_0$. Changing the variable by putting $\phi = \pi x/l_0$, we have:

$$i = \frac{2l_0}{\pi}\sqrt{1+K^2}\int_0^{\frac{\pi}{2}}\sqrt{1-\frac{K^3}{1+K^2}\sin^2\phi}\,.\,d\phi. \quad . \quad (2\,a)$$

Fig. 1.



From a table of the complete elliptic integral of the second kind numerical values of the integral in equation $(2\,a)$ were obtained and were used to plot the graph shown in fig. 1. The fractional extension (l/l_0-1) produced in a freely vibrating string due to its changing shape when sounding the fundamental tone only, is there plotted against the fractional amplitude (A/l_0). The assumptions used in the calculation are stated after equation (1).

If Y = Young's Modulus for the material of the wire, and r is the radius of the wire, the increase in tension δT is given by

$$\delta T = \pi r^2 Y(l/l_0 - 1).$$

On account of the high speed of propagation of longitudinal disturbances the variations of tension with position along the string may be neglected. It will be noted that (i.) the increase in tension is not directly proportional to the amplitude, and (ii.) the longitudinal component (along the axis of x) varies with a *frequency double that of the string's vibrations.* Perhaps the best experimental illustration of this second result is shown in a paper, "Photographs of Vibration Curves," by C. V. Raman (Phil. Mag. xxi. pp. 615–618, May 1911). The string used to obtain the photographs there shown had one end attached *normally* to a sounding-board, and the other end attached to a rigid support. When the string vibrated in a horizontal plane it was found that the motion of the sounding-board had a frequency strictly double that of the vibration of the string, no matter how the string had been excited. When, however, the vibrations took place in a vertical plane the fundamental appeared, due to the fact that the equilibrium position of the string was then a catenary and the change in length about the equilibrium position unsymmetrical. In the simultaneous vibration-curves of string and bridge photographically obtained from a monochord by E. H. Barton and J. Penzer (Phil. Mag. xiii. pp. 446–452, April 1907), the vibrations of double frequency are strongly present in the longitudinal motions of the bridge, although the fundamental can be detected in all the figures (see Pl. XI. figs. 7–13 and 27–39, also Pl. XII. figs. 40–47). The longitudinal displacement of the bridge was found to be about seventeen times the amplitude of the transverse motion. The motions of the violin bridge have been studied by E. H. Barton and T. F. Ebblewhite (Phil. Mag. xx. pp. 456–464, Sept. 1910), and were found to be still more complicated than the motions of the monochord bridges. The vibrations of double frequencies were sometimes present in the longitudinal motions, but other figures are shown in which a vibration much slower than that of the string is present (see, for example, Pl. IX. figs. 31, 37, 50, 60, 66, and 71). In a paper "On the

Pianoforte Bridges," by G. H. Berry (Phil. Mag. xxii. pp. 113–118, July 1911), two photographic records are given, fig. 3 showing the transverse vibrations of the "free" bridge, and fig. 4 the longitudinal vibrations; the latter are of strictly double the frequency of the former. It is of interest to note that the string was here stretched vertically. We shall return later to the consideration of the frequencies of the string's terminal forces.

Maximum Amplitudes and Tensions.—In order that a stretched string may behave elastically, it is necessary that its tension shall not exceed a certain value which is a constant for the material of the wire, although for a particular wire it depends also on the previous history of the wire. Hence, there is a theoretical limit to the amplitude of the vibrations of a string stretched with a given tension between firm supports. It is believed that the following considerations show the practical importance of a calculation of this theoretical limit. In the study of the struck string, it is found that the time of contact of the hammer and the string is usually some fraction of the period of the fundamental tone of the string. Hence, the whole of the energy communicated to the system has to be transferred from the hammer to the string in an exceedingly short time, which may well be one five-hundredth of a second, or less. Thinking now of the acoustics of the pianoforte, it is clear that either the loudness of the the sound or its duration, or both, will in a given instrument depend on the energy communicated to the system. The greater the tension, the greater the work done by the hammer in producing a given displacement of the string, and consequently for a given amplitude of vibration more energy can be given to the system. The length and linear density of the string can be adjusted to leave the pitch of the string unaltered without affecting the validity of these considerations. Hence we see the importance in pianoforte construction of using tensions as high as possible. Whether the increased supply of energy appears chiefly in louder sounds or in sounds of greater duration, will depend upon the construction of the sound-board and upon other considerations, studies of which by the present writer it is hoped to publish in later papers [see also Phil. Mag. xlviii. p. 42, July 1924]. It is of interest to note that in instruments involving the struck string the greatest difficulty has always been the communication of sufficient energy in a single blow to yield a sound sufficiently loud and sustained. The material used for the strings has been gut, silk prepared by a special process, latten, gold, silver, brass, iron, and, finally, steels of increasing tensile strength. In 1867, the breaking stress for carefully prepared steel wire of 0·77 mm. diameter was 226 lb. wt.; in 1893 this figure had been increased to 325 lb. wt. The increase in the tensions of the strings made possible by this increase in tensile strength resulted in a corresponding increase in intensity and duration of the tones. "It is not too much to say that the improvements in the tenacity and elasticity of steel wire made during the last century have rendered possible the modern piano," Wolfenden, 'Treatise on the Art of Pianoforte Construction,' 1916, p. 6.

If T be the original tension of the string, δT the maximum increase of tension due to the change of shape of the string when vibrating, and T′ the tension when the elastic limit is reached, then we may write for a maximum $T = T' - \delta T$. The value of T so found will then be the desirable tension for the particular wire in order that the energy of a vibration of given fractional amplitude may be a maximum. In Table I. are shown values of T for certain cases of practical interest, calculated from data given in Wolfenden (*loc. cit.* pp. 28–29), on the assumption that A/l_0 shall not exceed 0·01. The writer was unable to find numerical values for T′ for piano wire, but since the elastic limit, the yield point, and the breaking point are in this case close together, values of the breaking stresses have been used for T′. It will be noted that the original tension of all the strings here considered is the same. For a consideration of the factors which determine the tensions chosen for the strings of a pianoforte, the reader is referred to Wolfenden, *loc. cit.*, especially pp. 5–23, or to the 'Dictionary of Applied Physics,' iv. pp. 464–470.

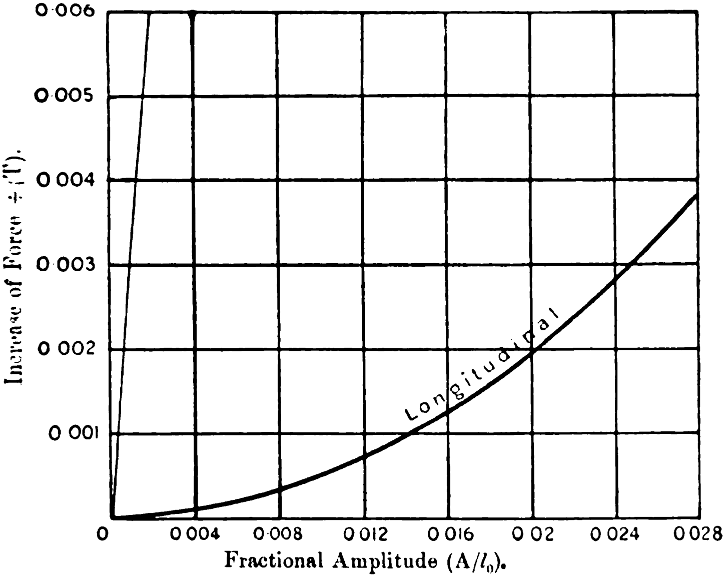
TABLE I.

Frequency.	l_0.	r.	δT.	T + δT.	Probable breaking tension ($\doteqdot$ T′).	T′ − (T + δT).
per sec.	cm.	cm.	dynes.	dynes.	dynes.	
4138·4	5·4	0·04	2·61 × 10^6	79·61 × 10^6	122·2 × 10^6	42·6 × 10^6
2069·9	10·2	0·0425	2·95	79·95	136·1	56·1
1034·6	19·25	0·045	3·31	80·31	147·7	67·4
517·3	36·4	0·0475	3·68	80·68	162·8	82·1
258·6	68·8	0·05	4·08	81·08	170·8	89·7
129·3	131·0	0·0525	4·49	81·49	182·4	100·9

INCLINATION OF THE STRING AT ITS ENDS.

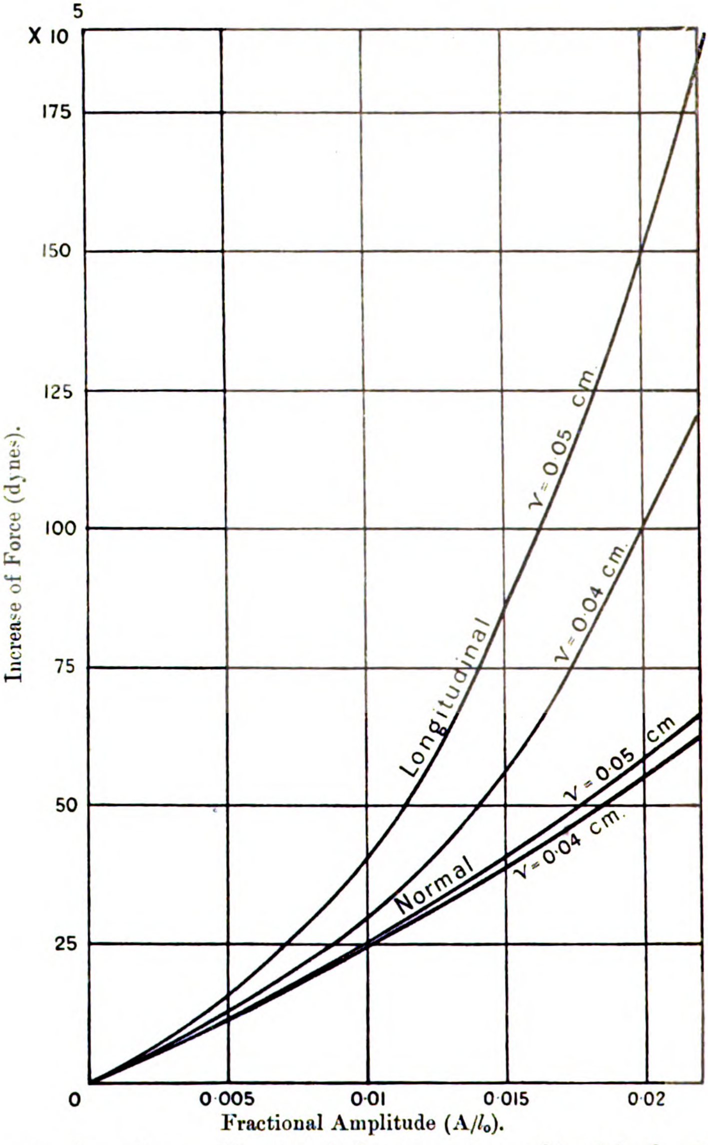
It is convenient to resolve the force due to the inclination of the string at its ends along and perpendicular to the equilibrium position of the string, since the rigidness of the supports actually used in experiments is usually most conveniently considered in these two directions. If the tension of the string be T_1 when the inclination of the string with its equilibrium position is ϕ, we have components $T_1 \cos \phi$ longitudinally and $T_1 \sin \phi$ normally. We may note that (i.) the longitudinal component is again of frequency double that of the string's vibrations, and (ii.) the inward force at the ends of the string is *decreased* when the string is displaced, this acting in opposition to the increased force due to the extension of the string. It would appear that the longitudinal component was much greater than the normal, but it should be remembered that when the string is at rest the longitudinal component is T, whilst the normal component is zero. We are, therefore, concerned rather with the component $(T_1 \cos \phi - T)$ which represents the *change* in the longitudinal force when the string is vibrating. In the lower curve of fig. 2, this component, divided by T, is plotted against the fractional amplitude (A/l_0). In the upper curve the (normal force) ÷ (T) is similarly plotted. Since in fig. 2 the tension

Fig. 2.



has been assumed constant, we see the influence of the inclination alone, whilst in fig. 1 we see the influence of the

Fig 3.



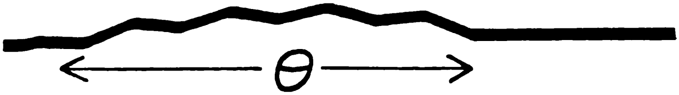
extension alone. The two influences are combined in fig. 3, which deals with two actual numerical examples, those of steel wires, for which $Y=20\times10^{11}$ dynes per sq. cm., $T=77\times10^6$ dynes, and $r=0\cdot05$ cm. and $0\cdot04$ cm. respectively. A length 68·8 cm. of the string for which $r=0\cdot05$ cm. would give a fundamental tone of frequency 258·6 per sec. The two upper curves deal with the longitudinal and the two lower with the normal components respectively. The importance of the longitudinal component of double frequency is clearly shown, but it should be noted that the audible vibrations do not usually proceed directly from the bridges, but from the sound-board to which the bridges are attached. The maintenance of a vibration by a force of double frequency, as, for example, in the longitudinal form of Melde's Experiment, is quite common, so that it may well happen that the longitudinal force of double frequency actually helps the maintenance of the single-frequency vibrations of the sound-board. It is hoped in a later paper to discuss the results of an experimental study of the motion of an actual sound-board, since in the accounts of the experimental work previously quoted there are not sufficient data concerning the mass and spring factors of the bridges there used, to enable one to calculate, for example, the theoretical amplitudes of vibration of the bridges.

STRUCK STRING DURING IMPACT.

So far, we have considered only the freely vibrating string. A curious point arises in connexion with a string struck near one end when we consider the frequency of the forces exerted by the string upon the nearer bridge during the impact. At the beginning the transverse disturbance travels outwards from the struck point along each of the two portions of the string. One-half of the disturbance soon reaches the nearer bridge, is there reflected, and again reaches the hammer. At the hammer it is reflected, and so on until the hammer quits the string. Since the duration of the impact is of the order of the fundamental period of the string [*i. e.* the time (θ) taken by the transverse disturbance to travel twice the length of the string], it follows that the disturbance is reflected a number of times at the nearer bridge. For instance, if the string be struck at $1/n$th of its length, and if the impact last for $\theta(n-1)/n$, then the nearer bridge receives $(n-1)$ impulses in the time $\theta(n-1)/n$. Hence we see that *if a string be struck near one end* at a point distant $1/n$th of its length from the nearer bridge, then, unless the duration of the impact be very near to the theoretical minimum, *the* nth *partial is encouraged at the nearer bridge.*

Fig. 4 shows a typical displacement-time curve of the initial motion of a point of the string between the hammer and the bridge. In this example the mass ratio (m/M) of hammer to string was unity, the length of the string was 316 cm., the struck point was distant 72 cm., and the observed point 35·2 cm. from the nearer bridge. The length along the time axis corresponding to the fundamental period (θ) of the string is indicated. The rapid impulses illustrated in the figure are of frequency 4·39 times that of the fundamental. The experimental details will be found in the second paper of this series (Phil. Mag. xlviii. pp. 34–37, July 1924).

Fig. 4.



It is believed that this anomalous encouragement of the nth partial by striking the string at $1/n$th of its length from one end is connected with a special feature of pianoforte construction. In laboratory experiments with the sonometer, the two bridges are equally important, and the system is approximately symmetrical about the mid-point of the string. In the pianoforte the vibrating length of the string is determined by one "fixed" bridge and one "free" bridge. The fixed bridge is a projection on the massive iron framework which sustains the huge combined tension of all the strings ; this bridge is not directly connected with the sound-board, and it plays but a small part in the communication of the string's vibrations to the sound-board. The free bridge is glued and screwed on to the sound-board itself, and is the more important in the communication of energy to the sound-board. Now, *the string is struck near the fixed bridge*, hence the initial rapid impulses of frequency n/θ (where n may or may not be a whole number) are not directly communicated to the sound-board.

It is hoped to publish in a later paper quantitative results of a study of the manner in which the forces considered in the present paper are able to produce the aerial vibrations actually heard when a string is coupled with bridges and sound-board of known properties and simple construction.

In conclusion, the writer wishes to thank Mr. F. Underwood, B.Sc., and Mr. N. Davy, B.Sc., for their kindness respectively in verifying the mathematics and checking one or two of the numerical calculations.

University College,
Nottingham,
Sept. 1924.

X. *On the Reflexion of Waves penetrating normally into a Stratified Medium.* By J. A. Wilcken, *B.Sc., Ph.D., Lecturer in Electrical Engineering at Armstrong College, Newcastle-upon-Tyne* [*].

THE question whether a gradual transition between two media of different refractive indices gives rise to any disintegration of an incoming wave-train, comparable to the reflexion in abrupt transition, has been the subject of much discussion. It is known that certain phenomena of polarization of reflected light are readily explained as due to a surface-film of varying index (*cf.* Maclaurin, 'Theory of Light,' Camb. 1908); and if that theory is adhered to, the possibility of a reflexion being caused by a continuous variation of properties must be admitted. It remains, however, to be examined whether a reflected wave is always set up in any variable medium, and to be determined on what characteristic qualities the intensity depends. The problem has acquired renewed importance in connexion with wireless signals of great wave-length.

The late Lord Rayleigh [†] has discussed in detail the problem of a vibrating string whose longitudinal density varies inversely as the square of the distance from one end, extending the application to phenomena other than those of sound, and concludes that reflexion is appreciable only when the transition is so sudden that the thickness of the variable layer is of the order of a wave-length; a later investigation [‡] deals with a medium built up of homogeneous strata of different qualities. From the standpoint of the electromagnetic theory of light, Gans [§] finds that within a certain range of approximation, characterized as "slow" transition and applicable in the domain of astrophysical optics, there is no reflexion; and Emden [||] discards the reflected wave completely, the legitimacy of his arguments being disputed by Wallot [¶]. An earlier controversy between Schmidt [**] and Seeliger [††] turns on a similar problem in solar physics.

It appears that previous writers have confined the discussion from the outset to a more or less specialized character of the transition; and the alternative method of approaching a continuously varying medium from the consideration of one built up of finite homogeneous strata has been strongly criticized by Uller*. It might therefore be of some interest to pursue a different line of investigation, with a view to establishing a general expression for the relative intensity of a reflected wave, without making any special assumptions except as to the reversibility implied in the linear equation of motion.

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[*] Communicated by the Author.

[†] Proc. Math. Soc. xi. pp. 51-56 (1880).

[‡] Proc. Roy. Soc. A, lxxxvi. pp. 207-226 (1912).

[§] *Ann. d. Phys.* xlvii. pp. 709-736 (1915).

[||] *Sitz. Ber. d. Bayr. Akad.* p. 417 (1918).

[¶] *Ann. d. Phys.* lx. pp. 734-762 (1919).

[**] *Phys. Zeitschr.* iv. pp. 282, 341, 453, 476 (1903); v. p. 67 (1904).

[††] *Ibid.* v. p. 237 (1904).

To avoid the complications arising from the change of direction involved in oblique incidence which I have discussed in a previous paper †, we consider a train of waves proceeding in the direction of positive x and impinging normally at the boundary, $x=0$, of a plane stratified medium, and take, as the equation of motion freed from the time-variable,

$$\frac{d^2U}{dx^2} + k^2U = 0, \quad . \ . \ . \ . \ . \ . \ . \quad (1)$$

where k is a real continuous function of x,

$$k = 2\pi/\lambda = 2\pi n\mu/c, \qquad k^{\,x \leq 0} = k_0.$$

The solution may be written, without loss of generality,

$$U = Ae^{\phi + i\psi} + Be^{\phi - i\psi}, \quad . \ . \ . \ . \ . \ . \quad (2)$$

where ϕ and ψ are real functions of x, satisfying the equations

$$\frac{d^2\phi}{dx^2} + \left(\frac{d\phi}{dx}\right)^2 - \left(\frac{d\psi}{dx}\right)^2 + k^2 = 0, \quad . \ . \ . \quad (3)$$

$$\frac{d^2\psi}{dx^2} + 2\frac{d\psi}{dx}\frac{d\phi}{dx} = 0. \quad . \ . \ . \ . \quad (4)$$

In the homogeneous medium $x < 0$ we have

$$U = He^{-ik_0x} + Ke^{ik_0x}, \quad . \ . \ . \ . \ . \ . \quad (5)$$

where H represents the amplitude of the incident positive wave, and K the amplitude of the reflected negative wave; supposing the variable medium bounded on the right by $x=x_1$, so that beyond this plane k retains the value it has at that point, $k\big|^{x>x_1} = k_1$, say, the solution for $x > x_1$ can be written

$$U = Ce^{-ik_1x}, \quad . \ . \ . \ . \ . \ . \ . \quad (6)$$

there being no reflected wave in the homogeneous medium $x > x_1$.

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* *Phys. Zeitschr.* xvii. pp. 369–373, (1916): xviii. pp. 35–41 (1917).

† Proc. Camb. Phil. Soc. xxii. pt. 2, pp. 124–131 (1924).

The boundary conditions of continuity require that

$$\frac{1}{\mathrm{U}}\frac{d\mathrm{U}}{dx}\bigg|^{-0} = \frac{1}{\mathrm{U}}\frac{d\mathrm{U}}{dx}\bigg|^{+0}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\frac{1}{\mathrm{U}}\frac{d\mathrm{U}}{dx}\bigg|^{x_1-0} = \frac{1}{\mathrm{U}}\frac{d\mathrm{U}}{dx}\bigg|^{x_1+0}; \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and, further,

$$\psi\,|^{0} = 0, \quad \frac{d\psi}{dx}\bigg|^{0} = k_0, \quad \frac{d\psi}{dx}\bigg|^{x_1} = k_1. \quad . \quad . \quad . \quad (9)$$

Writing now

$$\mathrm{K}/\mathrm{H} = \beta, \quad \mathrm{A}/\mathrm{B} = \alpha, \quad \frac{d\phi}{dx}\bigg|^{0} = f_0, \quad \frac{d\phi}{dx}\bigg|^{x_1} = f_1, \quad \psi\bigg|^{x_1} = \psi_1,$$

we have the conditions

$$-ik_0(1-\beta)/(1+\beta) = f_0 + ik_0(\alpha-1)/(\alpha+1), \quad . \quad . \quad . \quad . \quad (10)$$

$$-ik_1 = f_1 + ik_1(\alpha e^{i\psi_1} - e^{-i\psi_1})/(\alpha e^{i\psi_1} + e^{-i\psi_1}), \quad (11)$$

and find, from (11),

$$\alpha = -f_1 e^{-2i\psi_1}/(f_1 + 2ik_1), \quad . \quad . \quad . \quad . \quad (12)$$

which, on substituting in (10), gives

$$\beta = \frac{f_0 f_1(1-e^{-2i\psi_1}) + 2i(k_1 f_0 - k_0 f_1 e^{-2i\psi_1})}{-f_0 f_1(1-e^{-2i\psi_1}) - 2i(k_1 f_0 - k_0 f_1) - 4k_0 k_1} \quad . \quad (13)$$

symbolically; the ratio of the intensities of the reflected and incident waves becomes, after reduction,

$$|\beta|^2 = \mathrm{R}/(\mathrm{R} + 4k_0^2 k_1^2), \quad . \quad . \quad . \quad . \quad (14)$$

where

$$\mathrm{R} = (k_1 f_0 - k_0 f_1)^2 + f_0 f_1 \{(2k_0 k_1 + \tfrac{1}{2} f_0 f_1)(1-\cos 2\psi_1) + (k_1 f_0 - k_0 f_1)\sin 2\psi_1\}. \quad (15)$$

The phase-difference is

$$\delta = \tan^{-1}\frac{2(k_1 f_0 - k_0 f_1 \cos 2\psi_1) + f_0 f_1 \sin 2\psi_1}{f_0 f_1(1-\cos 2\psi_1) - 2k_0 f_1 \sin 2\psi_1} - \tan^{-1}\frac{2(k_1 f_0 - k_0 f_1) + f_0 f_1 \sin 2\psi_1}{f_0 f_1(1-\cos 2\psi_1) + 4k_0 k_1}.$$

It is seen from the expressions (14) and (15) that the reflected intensity depends mainly on the values f_0 and f_1, so that, if $f_1 = 0$, there is no reflexion in the variable medium, and the reflected wave in the medium $x<0$ depends entirely on the conditions at the boundary $x=0$; on the other hand, if $f_0=0$, the reflexion depends wholly on the boundary values k_1 and f_1; if both f_0 and f_1 are finite, the thickness of the layer comes in through the terms $1-\cos 2\psi_1$, $\sin 2\psi_1$, entailing a certain "fluctuation" of intensity, with minima for such values of x as make $\psi_1=m\pi$, m being any integer. It also appears, from the equation (4) and the condition (9), that f_0 and f_1 depend ultimately on the values of dk/dx at the boundaries, and this is brought out more clearly by the following.

The equations (3) and (4) may obviously be satisfied by taking

$$\frac{d\psi}{dx}=k, \quad \psi=\int_0^x k\,dx, \quad \text{and } \phi=-\tfrac{1}{2}\log k, \qquad (16)$$

provided

$$3\left(\frac{dk}{dx}\right)^2=2k\frac{d^2k}{dx^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

which is true, exactly, if

$$k=k_0(1+ax)^{-2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

If k is continuous, we may take the development

$$k=k_0+k'x+\ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

as correct to the first order for sufficiently small x, and we may also choose "a" in (18) so that the development

$$k_0(1+ax)^{-2}=k_0-2k_0ax+\ldots \quad . \quad . \quad . \quad (20)$$

will fit (19) as closely as we please. Hence, for sufficiently small x, we have

$$\frac{d\psi}{dx}=k,$$

$$\therefore \quad f_0=-\frac{1}{2k_0}\frac{dk}{dx}\Big|^0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

and a similar argument applies, on account of symmetry, to the boundary $x=a_1$.

It may therefore be inferred that reflexion from a continuously varying transition-layer depends primarily on the discontinuity of the gradient of the refractive index; if both the refractive index and its gradient are continuous throughout there is no reflexion. A similar conclusion was drawn by Gans for the approximate solutions discussed (*l. c.*), and is not contradictory to Lord Rayleigh's result in so far as the form of variation considered (*l. c.*) does not admit of a vanishing gradient for any finite x.

The form referred to corresponds, with a slightly different notation, to

$$k = k_0(1+ax)^{-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (22)$$

leading to

$$\phi = \tfrac{1}{2}\log(1+ax), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (23)$$

$$\psi = (k_0^2/a^2 - \tfrac{1}{4})^{1/2}\log(1+ax); \quad . \quad . \quad . \qquad (24)$$

and thus,

$$f = \tfrac{1}{2}a(1+ax)^{-1}$$

$$= -\frac{1}{2k}\frac{dk}{dx}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (25)$$

If the function defined by (18) be adopted, we obtain, as the general solution,

$$U = k^{-1/2}\left(Ae^{i\int_0^x k\,dx} + Be^{-\int_0^x k\,dx}\right), \quad . \quad . \qquad (26)$$

which may be used as approximate, in case $(dk/dx)^2$ and $k^{-1}\,d^2k/dx^2$ are small of the second order. This approximate solution has been discussed by Nicholson*. (*Cf.* also, Gans, *l. c.*)

Another case of interest is where

$$k = k_0 + k'x + \ldots$$

may be taken as correct to the first order, k' being small. The solution may be approached by writing

$$\phi + i\psi = \Phi = \pm ik_0x + px + \tfrac{1}{2}rx^2 + \ldots, \quad . \quad . \qquad (27)$$

where p and r are small constants of the first order. The function e^{Φ} will satisfy the equation (1), provided

$$\frac{d^2\Phi}{dx^2} + \left(\frac{d\Phi}{dx}\right)^2 + k^2 = 0, \quad . \quad . \quad . \quad . \quad . \qquad (28)$$

and on substituting, and equating to zero coefficients to like powers of x, the coefficients are found subject to the (approximate) conditions

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* Proc. Roy. Soc. A, lxxxi. pp. 286–299 (1908).

$$\left.\begin{aligned} \pm ik_0r + k_0k' &= 0, \\ r \pm 2ik_0p &= 0, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (29)$$

which are satisfied by taking

$$r = \pm ik' \qquad p = -k'/2k_0.$$

The solution may thus be written

$$U = e^{-k'x/2k_0}\{Ae^{i(k_0x+\frac{1}{2}k'x^2)} + Be^{-i(k_0x+\frac{1}{2}k'x^2)}\}. \quad . \quad (30)$$

We now have $f_0 = f_1 = -k'/2k_0$, and so the intensity ratio becomes

$$|\beta|^2 = \frac{k'^2\{(k_1-k_0)^2 + 2k_0k_1(1-\cos 2\psi_1)\}}{k'^2\{(k_1-k_0)^2 + 2k_0k_1(1-\cos 2\psi_1)\} + 16k_0^4k_1^2}, \quad (31)$$

neglecting, in this expression, cubes and higher powers of k'.

Introducing the refractive indices and taking $\mu_0 = 1$, we find

$$|\beta|^2 = \frac{\mu'^2(\mu^2 - 2\mu\cos 2\psi_1 + 1)}{\mu'^2(\mu^2 - 2\mu\cos 2\psi_1 + 1) + 64\pi^2n^3\mu^2/c^2}. \quad . \quad (32)$$

The reflected intensity is thus always small, as was to be expected from the assumed smallness of k', and it nearly vanishes for values of x such that

$$\psi = k_0x + \tfrac{1}{2}k'x^2 = m\pi,$$

or, in terms of the wave-length λ,

$$(2\pi/\lambda_0)(x - \lambda'x^2/2\lambda_0) = m\pi,$$

leading to

$$x = (\lambda_0/\lambda')(1 \pm \sqrt{1-4m\lambda'}). \quad . \quad . \quad . \quad (33)$$

Even a small change in the thickness of the layer may thus cause an appreciable relative change in the reflected intensity.

XI. *Note on the Application of the Ultramicrometer to the Microbalance.*

By R. WHIDDINGTON, *M.A., D.Sc., Cavendish Professor of Physics, and* F. A. LONG, *B.Sc., Assistant Lecturer in the University of Leeds*[*].

UP to the present the most sensitive microbalances which have been constructed are those of Steele and Grant[†], Ramsay and Gray[‡], and Pettersson[§]. In all cases, however, great sensitiveness has been obtained only at the expense of the maximum load and the general robustness of the apparatus, and the smallest change in weight measurable was of the order of one ten-millionth of the total load.

They have certain points in common. In each case the balance proper was made entirely of fused quartz, and enclosed in an airtight case, so that small changes in weight might either be compensated by or compared with the effective change in weight of a small air-bulb, produced by altering the pressure in the case. Deflexions of the beam were observed by the reflexion of a beam of light from a small mirror on the balance.

The first two, however, were supported by knife-edges, while the last was suspended by two very fine quartz fibres.

With the knife-edge type of balance the sensitiveness is no doubt limited by the sharpness of the knife-edge, but with the quartz suspensions, which work with no friction, the limit, as Pettersson suggests, appears to be imposed solely by the smallness of the tilt which can be measured by the optical device employed. Thus finally the problem resolves itself into one of measuring an extremely small distance, since the measurement of the distance moved through by the end of the beam amounts to the same thing as measuring the angle of tilt.

Now, the "Ultramicrometer"[||] devised by one of us provides a means of measuring distances of an extremely minute order.

This note is an account of an attempt to apply the "Ultramicrometer" to a balance of the Pettersson type.

Two possibilities were borne in mind: one being the construction of a balance of greater absolute sensitiveness than those mentioned, and the other being the construction of one of greater relative sensitiveness. Our experimental arrangements made it more convenient to attack the second problem first.

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[*] Communicated by the Authors.

[†] Proc. Roy. Soc. A. lxxxii. p. 580.

[‡] Proc. Roy. Soc. A. lxxxiv. p. 536.

[§] Proc. Phys. Soc. xxxii. p. 209 (1920).

[||] Phil. Mag. xl. p. 634 (1920).

Suppose that we have a balance with a beam about 9 cm. long, one end of which descends through a distance of the order of 10^{-3} cm. for an increase in weight of 10^{-6} gm. It was estimated that an ultramicrometer attachment, such as could be adapted to this balance, would measure a change of 2×10^{-7} cm., so that one might reasonably expect by this method to measure changes in weight of the order of 10^{-9} gm. with a much heavier balance than those mentioned, and hence a greater load.

Principle of the Instrument.

The "Ultramicrometer" has been fully described previously in this Magazine [*], but it may be mentioned that it consists essentially of two similar thermionic valve circuits capable of maintaining continuous oscillations of a frequency of some millions. The frequencies may be made to differ by such an amount that the beats produced by the two together give a note of audible frequency in a telephone receiver. Any slight change in capacity in one circuit produces a change in its frequency and hence a change in the frequency of the audible note.

In principle the method is merely to attach to each end of the balance light metal plates opposite and parallel to two fixed ones, thus in effect producing two condensers, one at each end of the beam.

A slight tilt of the beam has the effect of increasing one capacity while decreasing the other, the frequency of one circuit is thereby decreased and that of the other increased, so that the audible note changes. Incidentally, the total change is double what it would be if the movement were only applied to a condenser in one circuit.

Actually, of course, this arrangement involves two electrical connexions to the two plates on the beam. This is undesirable and is avoided in the final form of the instrument by a device described later.

General description of the Balance.

Fig. 1 is a diagrammatic sketch of the balance as actually used, with the case shown in section.

The balance is enclosed in a thick brass cylindrical case, provided with two windows (*a*). This case is flanged and ground on to a brass base, an airtight fit being obtained with the aid of a little rubber grease. Being too heavy to lift conveniently it is suspended by a wire passing over pulleys and its movement is controlled by the guide-rods (*d*).

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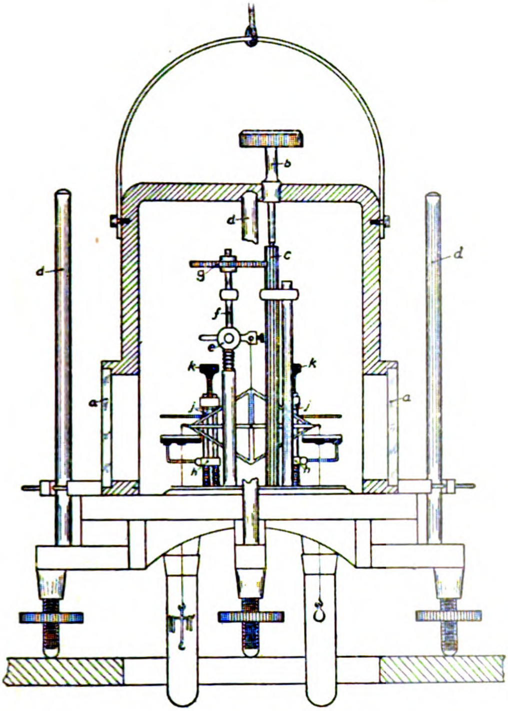
[*] *Loc. cit.*

Fig. 1.



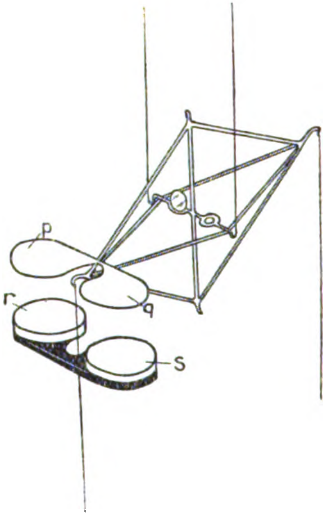
The beam, described more in detail later, is suspended from a horizontal rod capable of adjustment in two directions at right angles in a horizontal plane. The block (*e*) supporting this rod is made to move up and down the pillar (*f*) by the gear wheels (*g*), which are actuated from outside the case by the rod (*b*). The latter makes an airtight fit by means of a ground joint and engages in a slot in the rod (*c*).

Particular details embodied in the design.

(a) *The case.*—This is made of thick brass in order to minimize the effects of temperature changes.

(b) *The beam.*—On account of its physical properties fused quartz was used for the beam, as in other microbalances. The beam is shown separately in fig. 2. The central transverse rod has a small mirror cemented on one side, to permit of the use of a lamp and scale in the adjustment, and a tiny nut working on a fine screw cemented on the other side. This nut, which has a small projecting arm to enable it to be turned easily, is for rapidly making fine adjustments of the centre of gravity.

Fig. 2.



(c) *The suspension.*—The beam is suspended by two very fine quartz fibres, drawn out of the ends of the central transverse rod itself, and these are cemented to the support mentioned in the general description.

(d) *The air-weight and counterpoise.*—From each end of the beam a fibre ending in a hook is drawn. One carries a small air-bulb of about ·3 c.c. external volume, and the other a quartz counterpoise made in a form suitable for attaching additional quartz weights. These hang in closed glass tubes fitted by ground joints to the base. To make use of the air-weight the case of course has to be evacuated, so a side tube is provided and connected with an exhaust-pump and mercury manometer.

(e) *Condensers attached to the beam.*—To avoid any direct electrical connexion to the beam, the single condenser at each end, mentioned earlier, was replaced in the instrument as used by two condensers in series. Fig. 2 shows one pair of condensers only. The two middle plates (*p* and *q*) of each pair are cut from a single piece of aluminium sheet, as thin as possible consistent with rigidity, and cemented by the connecting portion to the beam. The two extreme plates (*r* and *s*) of each pair form the fixed plates, which are arranged under the connected plates and mounted on ebonite blocks. These blocks are connected by stiff ball and socket joints to metal blocks (*h*) moving on parallel pillars (*j*), and are moved by the screws (*k*). From the fixed plates leads pass through insulating plugs in the base to the inductances of the oscillating circuits.

The fixed plates also serve as an arrestment for the beam.

The Electrical Circuit.

The electrical circuit is essentially the same as that described in the account of the "Ultramicrometer"*, the condensers being incorporated with the balance, as explained above. Instead of putting the telephone-receiver directly in the plate circuits of the valves, a three-valve low-frequency amplifier and a loud-speaker were used. In order to bring the beat-note to a suitable audible frequency, a parallel plate air-condenser, one plate of which can be moved by a micrometer screw, was connected in parallel with the capacity in one of the valve circuits. Additional control can be obtained if necessary by varying the pressure in the case.

Setting up the Balance.

Setting up and adjusting the balance are operations requiring some patience, chiefly owing to the accidental breakage of one or other of the quartz fibres, and the fact that condenser plates have to be cemented to the beam.

Precautions necessary with the Electrical Circuits.

The extremely sensitive nature of the "Ultramicrometer" gives rise to certain difficulties which are briefly enumerated below, with the steps taken to minimize them.

(*a*) Mechanical vibration was prevented as far as possible by placing the apparatus on thick rubber corks on a rigid slate bench in a room in the basement. Even so, trouble was traced to movements and disturbances in other parts of the building and, in fact, outside it, so that it was found necessary to work very late at night or in the early morning.

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* *Loc. cit.*

(*b*) All leads were of stiff enamelled copper wire to prevent vibration.

(*c*) By suitably spacing the leads and portions of the apparatus stray capacity effects were minimized, as they might become appreciably large in the aggregate compared with the condensers used, thereby decreasing the sensitiveness.

(*d*) The apparatus was effectively screened against capacity changes due to movements of the observer by earthing the case and the negative side of the L.T. battery, and by enclosing other portions in earthed tin-lined cases.

(*e*) The batteries should be in excellent condition. A slight change in filament current alters the frequency *, but it is found that the current can be adjusted so that either an increase or a decrease produces a change of note in the same direction, *i. e.* this occurs at a turning point on a frequency filament-current curve (with anode voltage constant). The curve is fairly flat at this turning point, so that at this critical adjustment any slight fluctuation due to the batteries is less likely to affect the note.

There is a similar point on the frequency-anode voltage curve (with constant filament current) †, but in this particular instance it was not possible to take advantage of this fact owing to the necessity for keeping the anode voltage as low as possible, in order to minimize the electrostatic attraction between the plates.

(*f*) Soldered joints were used throughout.

(*g*) The cellar room temperature was found to be sufficiently constant for the experiment.

(*h*) Owing to the inequality in the separation of the condenser plates, there was an appreciable deflexion due to electrostatic attraction when the valves were switched on. This was made as small as possible by keeping the anode voltage low and by altering the pressure slightly until the plates were more equally spaced.

This additional force which is introduced into the balance system proved to be greater than expected, but as the plates can be almost equally spaced, and as the changes in weight it was desired to measure produce only a minute tilt, it did not interfere with the working of the balance.

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[*] Proc. Roy. Soc. A. xcvi. p. 455, and A. xcvii. p. 191.

[†] In some unpublished work carried out in this laboratory by Miss C. E. Watson, M.Sc., it was shown that the frequency falls to a minimum value and then rises again when the anode voltage is varied.

Method of using the Balance.

The centre of gravity was adjusted until the balance had a sensitiveness of the order mentioned earlier.

On varying the pressure the deflexion of the light-spot was found to be reasonably uniform, with the zero constant over a considerable period, showing however a slight creep in several days.

The constancy of zero was further tested by altering the anode voltage and bringing it back to its original value several times.

A long piece of very fine constantan wire was weighed and measured carefully, and a very small portion was cut off and measured. The change in pressure necessary to counterbalance this was used as the standard. It agreed sufficiently well with the value calculated from the volumes of the bulb and counterpoise.

A vessel of known capacity (about 1 litre) was also connected to the apparatus through a tap, and by measuring the change in pressure when this vessel was connected with the rest of the apparatus at various pressures, the internal volume of the case etc. could be calculated.

As a change of 1 mm. pressure produced a greater change in weight than was required, an additional adjustable manometer was attached and the bore of the fixed limb found. A small movement of the open limb produced a slight known change in volume from which the change in pressure could be calculated since the volume was known. The change in weight corresponding to this is known, so that we were able to produce changes in weight of the order desired. Of course the same end could have been attained by using a smaller bulb, but it was found more convenient to retain the larger bulb and use the method described.

With the valve circuits in action the note was adjusted to such a frequency that it gave a few beats per second with the note emitted by an audible frequency circuit used as standard, also provided with a loud-speaker so that the beats could be heard some distance away.

The pressure was then varied by steps over a small range, and the standard circuit adjusted each time by altering its capacity.

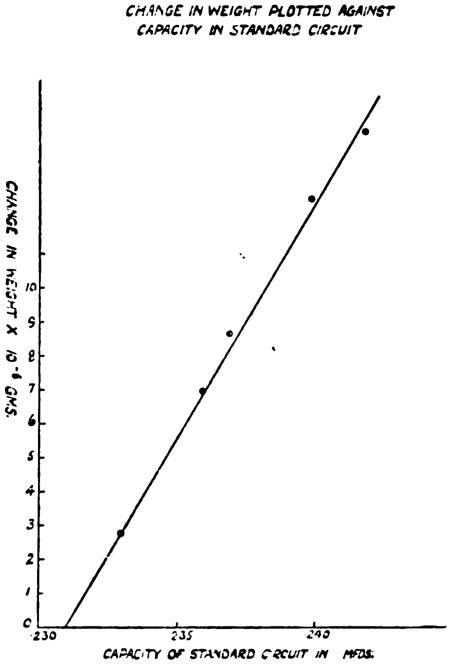
Results obtained.

As the note varies somewhat until the circuit has been left in operation for some minutes, time must be allowed for heat effects to become steady.

The slow beats were found to vary periodically about some mean, presumably owing to the natural swing of the balance which was unexpectedly persistent, and it was consequently impossible to count them. On this account the fullest use could not be made of the "Ultramicrometer" principle in the application of which the slow beat method is essential for highest accuracy.

The standard note was therefore adjusted to give the mean note each time the pressure was varied, and fig. 3 shows the kind of results obtained, where the change in weight is shown plotted against the corresponding capacity in the standard circuit. The points lie fairly well on a straight line, which is to be expected if the movement of the condenser plates is small compared with their separation.

Fig. 3.



The slopes of these lines are all practically the same, and the same note could be restored by returning the pressure to its original value.

The smallest change in weight which was used in obtaining the curves was $1{\cdot}67 \times 10^{-8}$ gm., which is rather less than one ten-millionth of the load, that is to say this arrangement is a few hundred times more sensitive than with a lamp and scale.

A change in weight of about 5×10^{-9} gm. produced an unmistakable change in the number each time, but since this change was of the same order as the variation of the note about the mean, it was impossible to *measure* it with any accuracy.

Conclusion.

Our experience indicates that if the slow beat method could have been used it would have been possible to measure a change of as little as 10^{-9} gm. or even less in a load of about 0·2 gm.

Unfortunately the practical difficulties have forced us to the conclusion that the instrument is not sufficiently simple in operation to be generally useful. Apart from this the balance is not sufficiently sensitive for the purpose for which it was originally designed.

We wish to thank Messrs. Ludbrook and Beecroft for their assistance in the workshop and Mr. L. G. Stanton for preparing the diagrams. Part of the cost of the balance was defrayed by a grant from the Royal Society.

Physics Laboratories,
University of Leeds,
September 1924.

XII. *On the Elastic Impact of the Pianoforte Hammer.*—II.

By S. Bhargava *and* R. N. Ghosh, *Department of Physics, Allahabad University**.

IN the June number of the 'Philosophical Magazine,' vol. xlvii., the authors have shown that the elasticity of the hammer felt must be taken into consideration for calculating the duration of impact. Kaufmann's approximate theory with the additional consideration of the elasticity of the hammer felt agrees fairly with the experimental results. In the present paper, calculation is made of the transmission of energy to the string by the elastic hammer, and the effect of stiffness upon the duration of impact has been shown to diminish it, whatever be the tension of the string. Finally, the law of pressure and the resulting amplitude of the partials have been calculated. It is found that Helmholtz's term plus two other terms are present, which are not insignificant.

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* Communicated by Prof. M. N. Saha.

2. *Calculation of the Communication of the Energy to the String.*

Helmholtz's Case.

In this case it is supposed that the impact is over before the disturbance produced by the hammer has travelled outwards. The pressure p has been shown to be given by

$$p = v_0(\mu \mathrm{M})^{\frac{1}{2}} \sin \{\mu/\mathrm{M}\}^{\frac{1}{2}}t, \qquad \ldots \ldots \qquad (1)$$

where v_0 is the initial velocity of the hammer. The duration of the impact is given by $\pi(\mu/\mathrm{M})^{-\frac{1}{2}}$. The displacement of the hammer is given by

$$y_0 = v_0(\mathrm{M}/\mu)^{\frac{1}{2}} \sin \{(\mu/\mathrm{M})^{\frac{1}{2}}t\}. \qquad \ldots \ldots \qquad (2)$$

The velocity of the hammer when it leaves the string is easily found to be the same as the initial velocity:

$$\text{Velocity of rebound} = -v_0.$$

Thus we see that in the ideal case of localized disturbance there should be no loss of energy by the hammer; but that energy is lost in producing waves in the piano string is beyond doubt: hence the assumption of no wave-motion during impact requires modification. The expressions (1), (2), and (3) are different from those derived by Mr. W. H. George*, who by introducing a new quantity, namely the velocity of rebound v, has obtained at $t=\frac{\mathrm{T}}{2}$ the value of maximum pressure,

$$p = \frac{\mathrm{M}\pi}{2\mathrm{T}} \cdot (v_0 + v),$$

where T is the duration of impact, while from (1) we obtain

$$p = \frac{v_0 \mathrm{M}\pi}{\mathrm{T}}.$$

Further, at $t=\frac{\mathrm{T}}{2}$ velocity of the hammer should be zero *when the pressure is maximum.* These facts are represented by (1) and (2), while George's expression gives for the velocity of the hammer at the same instant $\frac{1}{2}(v_0 - v)$. If, however, the above condition be imposed on Helmholtz's expression for the pressure,

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* Phil. Mag. xlvii. p. 596 (1924).

$$p = \mathrm{F} \sin \pi t/\mathrm{T},$$

$$\mathrm{F} = p_0 = \frac{v_0 \mathrm{M} \pi}{\mathrm{T}},$$

then George's equation (2) will be modified as follows :

$$\frac{dy}{dt} = v_0 + v_0(\cos \pi t/\mathrm{T} - 1),$$

from which it is evident that at $t = \mathrm{T}$ velocity of rebound is $-v_0$. It is the same as the initial velocity since the loss of energy of the hammer $= \frac{1}{2}\mathrm{M}v_1^2 - \frac{1}{2}\mathrm{M}v_2^2$, where v_1 and v_2 are velocities before and after impact. In this case $v_1 = v_2$, and therefore there is no loss.

In a case when the hammer spring is supposed to be bounded by a cylindrical surface which impinges upon the string, producing a localized dimple of the same size, we have

$$p = \mathrm{T}(8y/a)^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where a is the radius of the impinging cylinder. The equation of motion of the hammer is given by

$$\mathrm{M}\frac{d^2 y_0}{dt^2} = -p, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where p is the pressure between the hammer and the spring. Further,

$$p = \mu\xi \quad \text{and} \quad y_0 = y + \xi. \quad . \quad . \quad . \quad . \quad (5\,a)$$

y and y_0 are displacements of the string and hammer ; ξ is the compression and μ the strength of the spring. From (4), (5), and (5 a) we obtain to a first approximation,

$$y_0 = y + \alpha\xi^2,$$

where

$$\alpha = \frac{a\mu^2}{8\mathrm{T}^2} \quad \text{and} \quad (1 + 2\alpha\xi)\frac{d^2\xi}{dt^2} + 2\alpha\left(\frac{d\xi}{dt}\right)^2 + n^2\xi = 0,$$

where $n^2 = \mu/\mathrm{M}$.

For small values of α, an approximate solution for ξ is

$$\xi = v_0/n \sin nt - \frac{2\alpha v_0^2}{n^2}\cos nt + \frac{2\alpha v_0^2}{n^2}.$$

v_0 the initial velocity is supposed to be small compared with n.

The duration of impact is measured by the interval from the beginning of impact to the instant when the pressure is again zero. In this case it is $T = (\pi/n + 4\alpha v_0/n^2)$ and

$$\dot{y} = \frac{d\xi}{dt} + 2\alpha\xi\frac{d\xi}{dt}.$$

At $t=0$, $\dot{y}=v_0$ and $y=0$;

at $t=T/2$, $\dot{y}=0$ and $y=\frac{v_0}{n}\left(1+\frac{2\alpha v_0}{n}-\frac{16v_0\alpha^4}{n^4}+\ldots\ldots\right)$;

at $t=T$, $\dot{y}=-v_0$ and $y=0$.

Hence, when the hammer rebounds, no wrinkle is left in the string, and in this case, too, there is no loss of energy by the hammer. The case is different, however, when the wrinkle does not remain localized during impact.

Kauffmann's Case.

Kauffmann considered a case when the length of the string was finite and it was displaced during impact. He took the case when the striking distance α was small, but he regarded the hammer as hard. We have shown that the elasticity of the hammer felt must be taken into consideration. Regarding the hammer felt as equivalent to an elastic spring of strength μ, and neglecting terms of the order 10^{-3} in comparison with others, we obtain a solution for the case of the elastic hammer:

$$y = Ae^{-\frac{K}{2}t}\sin qt, \quad \ldots\ldots\ldots \quad (6)$$

$$q^2 = \left[\frac{T}{\alpha M_1}\left(\frac{\mu\alpha}{T+\mu\alpha}\right) - \tfrac{1}{4}K^2\right],$$

$$K = \frac{T}{M_1 C}\left(\frac{\mu\alpha}{T+\mu\alpha}\right), \quad \ldots\ldots\ldots \quad (7)$$

and

$$A = \frac{v_0}{q}\left\{1+\frac{T}{\mu}\left(\frac{1}{\alpha}-\frac{K}{2C}\right)\right\}^{-1}.$$

The duration of impact is approximately given by

$$\frac{\pi}{q} + \delta t,$$

where $\delta t = \alpha/C$ approximately.

Further,

$$y_0 = A\left(1+\frac{T}{\mu\alpha}\right)e^{-\frac{Kt}{2}}\sin qt \quad . \quad . \quad . \quad . \quad (8)$$

and
$$\frac{dy_0}{dt} = Be^{-\frac{Kt}{2}}\left\{q\cos qt - \frac{K}{2}\sin qt\right\},$$

where
$$B = A(1+T/\mu\alpha), \quad v_0 = Bq,$$

and v, the velocity of rebound,

$$= Bqe^{-\frac{\pi K}{2q}} \text{ approx.}$$

The energy absorbed by the spring

$$= \tfrac{1}{2}M_1v_0^2 - \tfrac{1}{2}M_1v^2$$
$$= \tfrac{1}{2}M_1A^2q^2(1-e^{-\frac{\pi K}{q}}) \text{ approx.}$$

The loss of energy in producing waves can be calculated by evaluating the potential energy of the wave-motion in the string. The equation of wave-motion is

$$\frac{d^2y}{dt^2} = C^2\frac{d^2y}{dx^2}.$$

Neglecting the effect of the reflexions from the shorter end, we must have

$$\text{at } x=\alpha, \quad y=Ae^{-\frac{Kt}{2}}\sin qt,$$
$$\text{and at } x=\infty, \quad y=0.$$

Assuming $y \propto e^{i(qt+Kit/2)}$,

$$\frac{d^2y}{dx^2} = -(q+iK/2)^2/C^2.y\,;$$

$$\therefore \quad y = Ae^{-\frac{K}{2C}(Ct-x+\alpha)}\sin\frac{q}{C}(Ct-x+\alpha). \quad . \quad (9)$$

This holds true only up to $0<t<l-\alpha/C$.

The total energy of wave-motion (kinetic plus potential)

$$= T\int_0^{CT}\left(\frac{dy}{dx}\right)^2 dx = \frac{\mu_1A^2q^2}{2}(1-e^{-\frac{\pi K}{q}}) \text{ approx.}$$

It is found that the energy is the same as lost by the hammer after impact.

3. *Effect of Stiffness on the Duration of Impact.*

The effect of stiffness on the free vibrations of a finite string has been investigated by the late Lord Rayleigh *.

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* 'Theory of Sound,' vol. i. art. 137.

He found out the increase in the potential energy due to stiffness, and then calculated the effect upon the periods. The same can, however, be done by an alternative method, which will be employed to evaluate the effect upon the duration of impact.

$$M = EI\frac{d^2y}{dx^2}, \quad \frac{dM}{dx} + F = 0.$$

M = bending moment, E = Young's modulus, I = moment of inertia of the cross-section perpendicular to the plane of bending, F = the shearing force.

The equation of motion of a stretched string now takes the form

$$\rho\frac{d^2y}{dt^2} = T\frac{d^2y}{dx^2} + \frac{\delta F}{\delta x}.$$

Assume

$$y \propto \sin\frac{s\pi x}{l}\,.\,\phi,$$

where ϕ is the normal coordinate.

$$\ddot{\phi} = -\frac{T}{\rho}\frac{s^2\pi^2}{l^2}\left\{1 + \frac{EI}{T}\frac{s^2\pi^2}{l^2}\right\}\phi,$$

$$T_s' = T_s\left\{1 - \frac{EI}{2T}\frac{s^2\pi^2}{l^2}\right\}, \quad \ldots\ldots \quad (10)$$

where T_s' is the period when stiffness is considered, and T_s is the period for a perfectly flexible string. Equation (10) is the same as formula (2) of art. 137 of Rayleigh's 'Theory of Sound,' vol. i.

Returning to our problem, we observe that

$$\left.\begin{aligned} y_1 &= \frac{yx}{\alpha} && 0 < x < \alpha, \\ y_2 &= f(Ct - x) && \alpha < x < l, \\ y &= f(Ct) && x = \alpha, \end{aligned}\right\} \quad \ldots\ldots \quad (10\,a)$$

and

$$p = \mu\xi = T\left\{\frac{y}{\alpha} + \frac{1}{C}\frac{dy}{dt}\right\} + F_1,$$

where F_1 is the shearing force due to stiffness on account of the change of inclination from y_1 to y_2 in the neighbourhood of the point struck.

$$M = EI\left\{\left(\frac{dy}{dx}\right)_1 - \left(\frac{dy}{dx}\right)_2\right\},$$

$$F = -\frac{dM}{dx} = EI\frac{d^2y}{dx^2} = \frac{EI}{C^2}\frac{d^2y}{dt^2}, \quad \ldots \quad (11)$$

where $\left(\frac{dy}{dx}\right)_1$ and $\left(\frac{dy}{dx}\right)_2$ are the inclinations on the two sides.

The equation (12)* is modified to the form

$$M_1\left(1+\frac{T}{\mu\alpha}-\frac{EI}{C^2M}\right)\frac{d^2y}{dt^2}+\frac{T}{C}\frac{dy}{dt}+\frac{Ty}{\alpha}$$

$$=-\frac{MT}{\mu C}\frac{d^3y}{dt^3}-\frac{EIM}{c^2\mu}\frac{d^4y}{dt^4}. \quad . \quad (12)$$

A full solution of (12) will be cumbrous, and so of little value. We shall be content with an approximate solution by neglecting terms which are comparatively small. The right-hand side can then be assumed to be zero. Then the solution is of the same form as before (equation 12, *loc. cit.*), but the numerical magnitude of q_s now comes out :

$$q_s^2-q^2=\frac{TEI}{C^2\alpha M^2}\left(\frac{\mu\alpha}{T+\mu\alpha}\right). \quad . \quad . \quad . \quad . \quad (13)$$

Hence we find that the direction of impact is decreased and that the diminution increases with I. For circular wire $I=\frac{\pi}{8}a^4$, so that the duration of the contact diminishes as the fourth power of the radius. Formula (13) shows that the duration of impact is always shortened, whatever be the nature of the hammer. Further, the effect is independent of tension.

4. *Calculation of the Law of Pressure.*

From (12) and (10 a) p is easily found to be

$$p=ATe^{-\frac{K}{2}t}\left\{\frac{\sin qt}{\alpha}+\frac{R}{C}\cos\overline{qt+\phi}\right\}, \quad . \quad . \quad (14)$$

where

$$R=(q^2-K^2/4)^{\frac{1}{2}} \quad \text{and} \quad \tan\phi=K/2q.$$

From (14) it is observed that the pressure on the string is not zero at the instant of impact. It is equal to TAq/C, and at the end of the interval π/q its magnitude is again the same, and becomes zero after a short interval δt obtained by putting $t=\pi/q+\delta t$ in (14). The fact that the pressure is not zero at the instant of impact is also confirmed by Professor Raman's curves†, where the hammer is considered to be perfectly hard. The interval δt is very small ; it is approximately equal to α/C. Hence we shall neglect it, and consider the duration of impact to be given by π/q

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* Phil. Mag. xlvii. p. 1145 (June 1924).

† Raman & Banerjee, Proc. Roy. Soc. xcvii. A, p. 105.

This amounts to neglecting the second term of equation (14); then the pressure is given by

$$p = \frac{\mathrm{AT}}{\alpha} e^{-\frac{\mathrm{K}}{2}t} \sin qt. \quad . \; . \; . \; . \; . \; . \quad (15)$$

5. *Calculation of the Intensity of the Partials.*

The equation of motion of a point on the string in terms of normal coordinates is given by

$$\ddot{\phi}_s + \left(\frac{s\pi\mathrm{C}}{l}\right)^2 \phi_s = \frac{2}{l\rho} \Phi_s,$$

where Φ_s is the generalized component of the force. And

$$\Phi_s = \mathrm{A} \sin \frac{s\pi\alpha}{l} e^{-\frac{\mathrm{K}}{2}t'} \sin qt'.$$

If ϕ_s and $\ddot{\phi}_s$ both be zero initially, then for $t > \frac{\pi}{q}$,

$$\phi_s = \frac{2\mathrm{A} \sin \frac{s\pi\alpha}{l}}{ln\rho} \int_0^{\frac{\pi}{q}} e^{-\frac{\mathrm{K}}{2}t'} \sin n(t-t') \sin qt' dt'$$

$$= \frac{2\mathrm{A} \sin \frac{s\pi\alpha}{l}}{ln\rho} \left[\frac{2q \cos \frac{n\pi}{2q} . \sin n\left(t - \frac{\pi}{2q}\right)}{q^2 - n^2} - \frac{\mathrm{K} \sin \frac{n\pi}{2q} \cdot \cos n\left(t + \frac{\pi}{2q}\right)}{2(q-n)^2} \right.$$

$$\left. + \frac{\mathrm{K}}{4} \frac{\pi}{q} \frac{\sin n\left(t + \frac{\pi}{q}\right)}{(q-n)} - \frac{\mathrm{K}\pi}{4q} \frac{\sin n\left(t - \frac{\pi}{q}\right)}{(q+n)} + \ldots \right] \text{ approx.}$$

[Notations follow Rayleigh's 'Theory of Sound,' vol. i. art. 134.]

The final solution for the displacement y becomes, when we substitute the value of n (to the same order of approximation),

$$y = \frac{2\mathrm{A}l^2}{\rho\pi\mathrm{C}} \sum_1^{\infty} \frac{\sin \frac{s\pi\alpha}{l} . \sin \frac{s\pi x}{l}}{s(lq - s\pi\mathrm{C})} \left\{ \frac{2q \cos\left(\frac{s\pi^2\mathrm{C}}{2lq}\right) \sin\left[\frac{s\pi\mathrm{C}}{l}\left(t - \frac{\pi}{2q}\right)\right]}{(lq + s\pi\mathrm{C})} \right.$$

$$- \frac{\mathrm{K}}{2} \frac{\sin\left(\frac{s\pi^2\mathrm{C}}{2lq}\right) . \cos\left[\frac{s\pi\mathrm{C}}{l}\left(t - \frac{\pi}{2q}\right)\right]}{(lq - s\pi\mathrm{C})} + \frac{\mathrm{K}}{4ql} \sin\left[\frac{s\pi\mathrm{C}}{l}\left(t + \frac{\pi}{q}\right)\right]$$

$$\left. - \frac{\mathrm{K}\pi}{4ql} . \frac{\sin\left[\frac{s\pi\mathrm{C}}{l}\left(t - \frac{\pi}{q}\right)\right]}{(lq + s\pi\mathrm{C})/(lq - s\pi\mathrm{C})} + \ldots\ldots \right\} . \quad . \; . \; . \; . \quad (16)$$

Equation (16) shows the first term obtained by Helmholtz and other terms which appear on account of finite displacement of the string during impact, but on account of the presence K of their magnitudes are small. The convergence of the first two terms is of the order s^{-3}, but the last two terms converge more slowly. They increase if K increases—that is, when the striking distance α increases.

For a given striking distance the first term disappears for those partials whose periods are 2/1, 2/3, 2/5, 2/7 of the duration of impact; but the other three terms do not disappear, hence the existence of a feeble intensity of them is explained.

When the point struck is very close to the first node of the sth component, then the sth component will be absent; but if at the same time the duration of impact $\frac{\pi}{q}=\frac{l}{Cs}$ approx. then $\sin\frac{s\pi^2C}{2lq}=1$ and $\sin\frac{s\pi\alpha}{l}$, $\cos\frac{s\pi^2C}{2lq}$ are both of the same order of smallness: the first term and the third term completely disappear, but the second term does not. Hence we find that a component having a node at the point struck is not entirely absent if the duration of impact is half the period of vibration of the component. Hipkins and others have found this experimentally to be true.

A given component will converge more rapidly the greater the value of q, which decreases as α increases. According to Helmholtz, however, the convergence is independent of the striking distance.

Conclusions.

These formulæ have been proposed tentatively, and the authors hope to verify them experimentally on a future occasion.

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XIII. *Note on the Problem of the Quantitative Formulation of Bohr's Correspondence Principle.* *By* RICHARD C. TOLMAN, *Ph.D., Professor of Physical Chemistry and Mathematical Physics at the California Institute of Technology*[*].

I. INTRODUCTION.

IT has been shown by Kramers[†] that the frequency of the light emitted when an atom passes from one quantum state to another may be regarded as an average of the frequencies which would be emitted, on the basis of the classical theory, by the various mechanically possible states intermediate between the initial and final quantum states. Bohr's principle of correspondence indicates that the intensity of the light emitted should also be calculable by a suitable average of the intensities which would be emitted by these intermediate states on the basis of the classical theory. In two recent articles, Hoyt[‡] has used six possible methods of obtaining this average, including one suggested by Kramers, to calculate the relative probabilities of transitions between various pairs of quantized Kepler orbits, and has tried to test his results by data on the intensity of X-ray and Balmer series lines. Unfortunately, the experimental information available was not sufficient to permit a definite decision as to the proper method of averaging

It is the purpose of this note to present the results obtained by using these different methods of averaging, to calculate the probability of transitions in the case of three very simple quantum systems with only a single degree of freedom—namely the harmonic oscillator, the rotating dipole, and the simplified hydrogen atom with circular orbits. These systems are so simple that the calculations can be made without approximations, and the significance of the results can perhaps be more readily appreciated than in more complicated cases. It is a matter of interest that only one of the methods of averaging leads to the value zero for the probability that an electron will fall into the nucleus from the innermost orbit in the hydrogen atom, the other methods leading to an infinite value for this probability.

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[*] Communicated by the Author.

[†] Kramers, *Kgl. Danske Vidensk. Selsk. Skifter*, 8. Raekke, iii. 3, p. 327.

[‡] Hoyt, Phil. Mag. xlvi. p. 135 (1923); *ibid.* xlvii. p. 826 (1924).

II. THEORY OF THE CALCULATION.

Consider the transition of a system of *one degree of freedom* between two stationary quantum states S' and S'', which have for the phase integral ($\oint p\,dq$) the values

$$I' = n'h \quad \text{and} \quad I'' = n''h, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n' and n'' are the quantum numbers corresponding to the initial and final states, and h is Planck's constant. Let the value of the phase integral for mechanically possible intermediate states be given with the help of the auxiliary variable λ by the equation

$$I = I'' + \lambda(I' - I''), \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where λ can assume values between unity and zero.

In accordance with the equation of Kramers, the frequency ν of the light emitted by the transition is connected with the frequency $\tau\omega$ of the corresponding harmonic in the Fourier expansion for the motion of the atom by the expression

$$\nu = \int_{\lambda=0}^{\lambda=1} (\tau\omega)\,d\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the corresponding harmonic is the one in which the order number τ is related to the quantum numbers n' and n'' by the equation

$$\tau = n' - n'', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and the fundamental frequency ω in the motion of the atom is related to energy E and phase integral I by the classical equation

$$\omega = \frac{dE}{dI}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

On the basis of the classical theory, the average rate of energy emission corresponding to the τth harmonic and a particular direction of polarization would be

$$\left(\frac{dR}{dt}\right)_{\text{Cl.}} = gC_{\tau}^{2}\tau^{4}\omega^{4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where the proportionality constant g has the value $16\pi^4/3c^3$, and the quantity C_τ is the amplitude of the τ'th harmonic in the Fourier analysis of the expression for the electric moment of the atom in the direction of polarization under consideration. On the basis of the quantum theory, the average rate of energy emission corresponding to a particular transition would be

$$\left(\frac{dR}{dt}\right)_{\text{Qu.}} = A_{\prime}^{\prime\prime}\,h\nu, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $A_{\prime}''$ is the probability, as introduced by Einstein, that the atom will make the transition in question in unit time. In accordance with the correspondence principle, we should expect the quantum theory expression to be some form of average of the classical expression which might be expressed by the equation

$$A_{\prime}'' h\nu = \sum_{x, y, z} [g C_{\tau}^2 \tau^4 \omega^4]_{\text{av.}}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where the summation sign indicates the necessity of taking into account the amplitude of oscillation parallel to each of the three axes. Or, if in accordance with the spirit of the correspondence principle * we take Q as the amplitude of the "virtual oscillators" of frequency ν, which for the purposes at hand could be substituted for the atoms, we might write

$$A_{\prime}'' h\nu = \sum_{x, y, z} [g Q^2 \nu^4] = \sum_{x, y, z} [g C_{\tau}^2 \tau^4 \omega^4]_{\text{av.}}. \quad . \quad . \quad (9)$$

The following six possible methods of performing the indicated average, and thus determining the amplitude Q of the "virtual oscillator," are the ones to be investigated :—

$$Q^2 = \int_0^1 C_{\tau}^2 \, d\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

$$Q = \int_0^1 C_{\tau} \, d\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

$$\log Q = \int_0^1 \log C_{\tau} \, d\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (C)$$

$$Q^2 \nu^4 = \int_0^1 C_{\tau}^2 \tau^4 \omega^4 \, d\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (D)$$

$$Q \nu^2 = \int_0^1 C_{\tau} \tau^2 \omega^2 \, d\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (E)$$

$$\log (Q\nu^2) = \int_0^1 \log (C_{\tau} \tau^2 \omega^2) \, d\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad (F)$$

III. EXPRESSIONS USED IN THE CALCULATIONS.

In order to perform the indicated integrations, we shall have to express amplitude C_{τ} and frequency of motion ω in terms of the auxiliary variable λ. This can be easily done, however, since the relation between the phase integral I and the variable λ is given by equation (2), and C_{τ} and ω are completely determined when the value of I is known.

We give below, for the three systems considered, all that

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* See Bohr, Kramers, and Slater, Phil. Mag. xlvii. p. 785 (1924).

remains of the Fourier expansions for the electric moments ξ, η, and ζ parallel to the three axes, the amplitude C and frequency of motion ω for mechanically possible motions lying between the states determined by the quantum numbers n and $n+1$, and the frequency ν of the light emitted by a quantum transition from $n+1$ to n. For convenience, the results are expressed in terms of the quantities C_1 and ω_1, which are the amplitude and frequency of motion in the quantum state where n equals unity.

1. *The Linear Harmonic Oscillator.*

$$\xi = C\cos 2\pi\omega t, \qquad \eta = \zeta = 0\,;$$
$$C = (n+\lambda)^{1/2}C_1\,;$$
$$\omega = \omega_1\,;$$
$$\nu = \omega_1.$$

2. *The Rigid Dipole Rotator.*

$$\xi = C\cos 2\pi\omega t, \quad \eta = C\cos\left(2\pi\omega t+\frac{\pi}{2}\right), \quad \zeta = 0\,;$$
$$C = C_1\,;$$
$$\omega = (n+\lambda)\,\omega_1\,;$$
$$\nu = \frac{(2n+1)}{2}\,\omega_1.$$

3. *The Simplified Hydrogen Atom (Electron in Circular Orbit).*

$$\xi = C\cos 2\pi\omega t, \quad \eta = C\cos\left(2\pi\omega t+\frac{\pi}{2}\right), \quad \zeta = 0\,;$$
$$C = (n+\lambda)^2C_1\,;$$
$$\omega = \frac{\omega_1}{(n+\lambda)^3}\,;$$
$$\nu = \frac{2n+1}{n^2(n+1)^2}\,\frac{\omega_1}{2}.$$

RESULTS OF THE CALCULATIONS.

The results of the calculations for the three systems are presented in tabular form. The first column gives the method of averaging employed; the second column the square of the amplitude of the "virtual oscillator," Q^2, corresponding to the transition from quantum number $n+1$ to n; the third column the probability, A^n_{n+1}, that this transition will occur in unit time; and the last two columns the values assumed by these two quantities for the special case of the transition from quantum number one to zero.

1. *The Linear Harmonic Oscillator.*

Method of Average.	Q^2 $n+1\to n$.	A^n_{n+1}.	Q^2 $1\to 0$.	A_1^0.
A and D.	$\frac{2n+1}{2}C_1^2$	$\frac{2n+1}{2}\frac{g}{h}C_1^2\omega_1^3$	$\frac{1}{2}C_1^2$	$\frac{1}{2}\frac{g}{h}C_1^2\omega_1^3$
B and E.	$\frac{4}{9}\{(n+1)^{3/2}-n^{3/2}\}^2C_1^2$	$\frac{4}{9}\{(n+1)^{3/2}-n^{3/2}\}^2\frac{g}{h}C_1^2\omega_1^3$	$\frac{4}{9}C_1^2$	$\frac{4}{9}\frac{g}{h}C_1^2\omega_1^3$
C and F.	$\frac{1}{\epsilon}\frac{(n+1)^{n+1}}{n^n}C_1^2$	$\frac{1}{\epsilon}\frac{(n+1)^{n+1}}{n^n}\frac{g}{h}C_1^2\omega_1^3$	$\frac{1}{\epsilon}C_1^2$	$\frac{1}{\epsilon}\frac{g}{h}C_1^2\omega_1^3$

2. *The Rigid Dipole Rotator.*

Method of Average.	Q^2 $n+1\to n$.	A^n_{n+1}.	Q^2 $1\to 0$.	A_1^0.
A, B, and C.	C_1^2	$2\times\frac{(2n+1)^3}{8}\frac{g}{h}C_1^2\omega_1^3$	C_1^2	$2\times\frac{1}{8}\frac{g}{h}C_1^2\omega_1^3$
D.	$\frac{16}{5}\frac{(n+1)^5-n^5}{(2n+1)^4}C_1^2$	$2\times\frac{2}{5}\frac{(n+1)^5-n^5}{2n+1}\frac{g}{h}C_1^2\omega_1^3$	$\frac{16}{5}C_1^2$	$2\times\frac{2}{5}\frac{g}{h}C_1^2\omega_1^3$
E.	$\frac{16}{9}\frac{\{(n+1)^3-n^3\}^2}{(2n+1)^4}C_1^2$	$2\times\frac{2}{9}\frac{\{n+1)^3-n^3\}^2}{2n+1}\frac{g}{h}C_1^2\omega_1^5$	$\frac{16}{9}C_1^2$	$2\times\frac{2}{9}\frac{g}{h}C_1^2\omega_1^3$
F.	$\frac{16}{\epsilon^4}\frac{(n+1)^{4(n+1)}}{n^{4n}(2n+1)^4}C_1^2$	$2\times\frac{2}{\epsilon^4}\frac{(n+1)^{4(n+1)}}{n^{4n}(2n+1)}\frac{g}{h}C_1^2\omega_1^3$	$\frac{16}{\epsilon^4}C_1^2$	$2\times\frac{2}{\epsilon^4}\frac{g}{h}C_1^2\omega_1^3$

3. *The Simplified Hydrogen Atom (Electron in Circular Orbit).*

Method of Average.	Q^2 $n+1\rightarrow n$.	A^n_{n+1}.	Q^2 $1\rightarrow 0$.	A_1^0.
A.	$\frac{1}{5}\{(n+1)^5-n^5\}C_1^2$	$2\times\frac{1}{40}\frac{\{(n+1)^5-n^5\}(2n+1)^3}{n^6(n+1)^6}\frac{g}{h}C_1^2\omega_1^3$	$\frac{1}{5}C_1^2$	∞
B.	$\frac{1}{9}\{(n+1)^3-n^3\}^2C_1^2$	$2\times\frac{1}{72}\frac{\{(n+1)^3-n^3\}^2(2n+1)^3}{n^6(n+1)^6}\frac{g}{h}C_1^2\omega_1^3$	$\frac{1}{9}C_1^2$	∞
C.	$\frac{1}{\epsilon^4}\frac{(n+1)^{4(n+1)}}{n^{4n}}C_1^2$	$2\times\frac{1}{8\epsilon^4}\frac{(n+1)^{4n-2}(2n+1)^3}{n^{4n+6}}\frac{g}{h}C_1^2\omega_1^3$	$\frac{1}{\epsilon^4}C_1^2$	∞
D.	$\frac{16}{7}\frac{n(n+1)\{(n+1)^7-n^7\}}{(2n+1)^4}C_1^2$	$2\times\frac{2}{7}\frac{\{(n+1)^7-n^7\}}{n^5(n+1)^5(2n+1)}\frac{g}{h}C_1^2\omega_1^3$	0	∞
E.	$\frac{16}{9}\frac{n^2(n+1)^2\{(n+1)^3-n^3\}^2}{(2n+1)^4}C_1^2$	$2\times\frac{2}{9}\frac{\{(n+1)^3-n^3\}^2}{n^4(n+1)^4(2n+1)}\frac{g}{h}C_1^2\omega_1^3$	0	∞
F.	$16\epsilon^8\frac{n^{8(n+1)}}{(n+1)^{8n}(2n+1)^4}C_1^2$	$2\times 2\epsilon^8\frac{n^{8n+2}}{(n+1)^{8n+8}(2n+1)}\frac{g}{h}C_1^2\omega_1^3$	0	0

IV. DISCUSSION OF RESULTS.

It is a matter of interest that all the methods of averaging, with the exception of F, lead to an infinite probability that an electron in the innermost orbit of the hydrogen atom would fall during unit time into the nucleus. On the other hand, method F leads to what we must regard as experimentally correct—namely zero for the chance that the electron would fall into the nucleus *.

Although this result would seem somewhat strong evidence against all except method F, attention should be called to the fact that the treatment given can hardly be regarded as absolutely exact, since it assumes that the inverse square law of attraction would hold down to zero distance between nucleus and electron—an assumption which does not agree with the finite mass and hence finite energy of the hydrogen atom. Furthermore, it should be noted that Hoyt's results seemed unfavourable to method F. Further work on the problem is much to be desired †.

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July 24th, 1924.

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* If we are permitted to trespass for a moment in a field of visionary speculation, it is interesting to note that although method F leads to zero for the chance that an electron would fall into the nucleus during unit time, it leads to a finite value, $2\epsilon^8 y C_1^2 \omega_1^4$, for the rate at which energy would be emitted by hydrogen atoms in the first quantum orbit, since the vanishingly small number of transitions is multiplied by the infinite energy emitted in each transition. This result might have astrophysical significance in connexion with the difficulty of discovering a sufficient source for the energy emitted by some of the stars. The falling of an electron into the hydrogen nucleus would presumably lead to the destruction of the atom with the production of an amount of radiant energy equivalent to its mass. The fact that our treatment would make the energy emitted infinite when an electron falls into the nucleus may not seriously affect the approximate correctness of our figure for the rate of energy emission.

† The writer wishes to express his thanks to Mr. I. S. Bowen for his kindness in reading the manuscript and checking the calculations involved in the above article. Mr. Bowen has also made an interesting generalization as to the results of different methods of averaging. If we take $\log(Q\nu^x)=\int_0^1 \log(C\omega^x)\,d\lambda$, then it can be shown that the condition $x>1{\cdot}5$ will make the probability zero that an electron in the first orbit will fall into the nucleus. If we take $Q^x\nu^y=\int_0^1 C^x\omega^y\,d\lambda$, then we may distinguish two cases. When $2x+1>3y$, we must have $3x<2y$ in order to make the above probability zero. When $2x+1<3y$, we must have $x+y<1$ to make the probability zero.

XIV. *The Period of Mesothorium 2.* *By* W. P. Widdowson, *B.A., Scholar of Christ Church, Oxford, and* A. S. Russell, *M.A., D.Sc., Dr. Lee's Reader in Chemistry* *.

MESOTHORIUM 2 was discovered in 1908 by O. Hahn †, who found its half-value period to be 6·2 hours. McCoy and Viol ‡ found the value 6·14 hours. Recently in an unsuccessful attempt to isolate a second product of mesothorium 1, corresponding to mesothorium 2 as uranium Z does to uranium X_2, we made several determinations of mesothorium 2's period. Our mean value is 5·95 hours, which is four per cent. smaller than Hahn's.

In chemical properties mesothorium 2 (atomic number 89) resembles the rare earths and is usually described as being similar to lanthanum. When fractionated along with the rare earths its isotope actinium appears to be concentrated in the neodymium and samarium fractions § so that they are homologues of the missing element of atomic number 61. In qualitative analysis mesothorium 2 is precipitated as hydroxide by ammonia, but quantitatively only in absence of a moderate quantity of ammonium salts. Its parent substance, mesothorium 1, when very concentrated contains radium and therefore also products both of the thorium and the radium series. The separation of mesothorium 2 from mesothorium 1 (atomic number 88) has consequently to be carried out in the presence of products of atomic numbers 90 (radiothorium), 88 (radium, thorium X), 86 (radon, thoron), 84 (radium A, thorium A, etc.), 83 (radium C, thorium C), and 82 (radium B, thorium B). There is, however, no difficulty in this.

The procedure we found best was as follows:—First we precipitated products of atomic numbers 90, 89, 84, 83, and 82 from those of atomic number 88 by dissolving a preparation of mesothorium bromide, equal in γ-ray activity to 6 mgrms. $RaBr_2$, in water, adding to the solution another containing the nitrates of lanthanum, thorium, and barium, and precipitating with carbonate-free ammonia. Mesothorium and its isotopes alone remain in solution with the barium. This solution was then acidified and set aside for a time. It lost radon and thoron freely so that their products soon decayed to a negligible concentration. After a month

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[*] Communicated by the Authors.

[†] O. Hahn, *Phys. Zeit.* ix. p. 246 (1908).

[‡] H. N. McCoy & C. H. Viol, Phil. Mag. xxv. p. 333 (1913).

[§] A. Debierne, *Compt. rend.* cxxxix. p. 538 (1904).

the concentration of thorium X had fallen to about 0·004 of its original value, mesothorium 2 had attained its equilibrium amount, and a small quantity of radiothorium had grown. A small quantity of thorium, free from all products but radiothorium, was then added, and precipitated from solution by carbonate-free ammonia. This removed all radioactive products from the solution except isotopes of mesothorium 1. The filtrate was acidified, a small quantity of thorium added to it, and half-an-hour later the thorium was precipitated by ammonia. This thorium precipitate was found to contain mesothorium 2 only which had grown in the interval, for the β-ray activity decayed exponentially with a period of about six hours, and the residual activity was very small.

Several determinations of the half-value period were carried out by freeing the active solution from mesothorium 2, allowing this product to accumulate for times which varied from seven minutes to twenty-four hours, and precipitating it along with thorium with ammonia. (Thorium was used instead of lanthanum as a nucleus for the active material because it is precipitated by ammonia even in presence of a large amount of ammonium salts, and in the active solution employed these were accumulating. It was prepared free from all its products except radiothorium by adding to a solution of it, a solution of lead, bismuth, lanthanum, and barium nitrates, almost removing the acidity by ammonia, and precipitating the thorium with excess of a solution of *m*-nitrobenzoic acid. The thorium so precipitated is entirely free from all its products.) The thorium precipitate containing the mesothorium 2 was washed, dried, ignited, and its activity observed in a β-ray electroscope. These observations occupied about five minutes. In none of the preparations was any initial abnormal decay observed; the active material decayed exponentially to zero. In seven of the best experiments the following values of the half-value period in minutes were obtained :—360, 352, 359, 361, 356, 354, and 356. The mean value is 357 minutes or 5·95 hours. The period of average life is consequently 8·58 hours, and the disintegration constant λ is 0·116 per hour. This value of the half-value period is probably within 3 minutes of the true value and is 15 minutes less than Hahn's.

The experiments described show that there is no appreciable quantity of another product of mesothorium 1, isotopic with mesothorium 2, if such has a period between 3 minutes and 6 hours. For a hypothetical product with these properties would become concentrated in mesothorium 2 by an operation which removed them entirely from solution and then allowed them to grow for an interval of time which is of the same order as the period of the more quickly-changing product. This product should then be revealed by an initially abnormal decay of the separated products. For example, supposing that the hypothetical product has a period of 7 minutes, and that in equilibrium it emits one β-particle for every 500 β-particles emitted by mesothorium 2. After both have been removed from a solution of mesothorium 1 and allowed to grow for 7 minutes, the ratio is raised from 1 : 500 to 1 : 10. Seven minutes later when these products have been separated from the solution and are ready for measurement in the electroscope the ratio has fallen to 1 : 20, but this is high enough to allow the presence of the minor but more quickly-changing constituent to be shown by the measurements of decay. The closer the periods of the isotopic products, the greater must be the proportion of the minor constituent in the mixture to make detection possible. In none of the experiments which we carried out was any trace of a minor isotope revealed. If, however, such an isotope had a period of about 2 minutes or less it would have escaped us unless its concentration was considerable, for 5 or 6 minutes was necessary to filter off the products and prepare them for the electroscope.

If the hypothetical product had a period considerably larger than that of mesothorium 2 it would be found in appreciable concentration only in the first precipitate of lanthanum and thorium hydroxides from the original solution of mesothorium. This precipitate was dissolved in acid, a solution of lead and barium nitrates added to it, and the lanthanum separated from the lead by sulphuretted hydrogen, from the barium by carbonate-free ammonia, and from the thorium by *m*-nitrobenzoic acid. The intensely active precipitate was then allowed to decay for several days until mesothorium 2 had attained a negligible concentration, and examined from time to time to see if a long-lived isotope was present. A small quantity of a β-ray body remained, but this proved to be, by its emanating power and period, thorium X, doubtless either adsorbed by the lanthanum or precipitated in small amount by ammonia in presence of air. This substance was dissolved in acid, a solution of barium nitrate added to it, and carbonate-free ammonia added in excess. These operations were repeated. The concentration of thorium X in the precipitated lanthanum was then found to be negligible. There appears then to be no appreciable amount of a second product of mesothorium 1 with a longer period than that of mesothorium 2 in the preparation with which we worked. Our preparation was one that had a γ-ray activity equal to that of 6 milligrams of radium bromide. Naturally before such a question can be settled more active preparations must be examined.

Summary.

1. A strong source of mesothorium was examined to see if it gave a branch product isotopic with mesothorium 2. It is found that no second product with a period smaller than that of mesothorium 2 exists in any detectable amount. Preliminary experiments indicate that the existence of a product with a greater period is also unlikely.

2. The half-value period of mesothorium 2 has been measured accurately. It is 5·95 hours. This value is probably less than one per cent. in error. It is four per cent. smaller than Hahn's original value, 6·2 hours. The new value of the disintegration constant is 0·116 per hour.

A grant from the Government Grant Committee of the Royal Society kindly made to one of us was used in purchasing materials for this piece of work.

Dr. Lee's Laboratory,
Christ Church, Oxford.
October 1924.

XV. *Note on the Poynting-Flux in a Gradually Varying Dielectric.* *By* J. A. Wilcken, *B.Sc., Ph.D., Lecturer in Electrical Engineering at Armstrong College, Newcastle-upon-Tyne* [*].

IN connexion with the transmission of energy along high-tension cables the problem has arisen of the influence of grading, or variation of the dielectric constant of the insulating material, on the Poynting-Flux.

To approach the problem, we consider a plane stratified medium, in which the dielectric constant ϵ, and the permeability μ, are real continuous functions of x, and take the medium bounded to the left by the plane $x=0$. A train of plane waves impinges on the boundary, coming from $x<0$, and we consider first the case of polarization in the incidence-plane xy.

Maxwell's equations, connecting the components X, Y, Z, of the electric force, and α, β, γ of the magnetic force, become

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[*] Communicated by the Author.

$$\left.\begin{aligned} \epsilon\frac{\partial Z}{\partial t}&=\frac{\partial\beta}{\partial x}-\frac{\partial\alpha}{\partial y}\\ -\mu\frac{\partial\alpha}{\partial t}&=\frac{\partial Z}{\partial y}\\ \mu\frac{\partial\beta}{\partial t}&=\frac{\partial Z}{\partial x}\end{aligned}\right\}\quad\ldots\ldots\quad(1)$$

Differentiating the first equation, we find

$$\epsilon\frac{\partial^2 Z}{\partial t^2}=\frac{\partial}{\partial x}\left(\frac{1}{\mu}\frac{\partial Z}{\partial x}\right)+\frac{1}{\mu}\frac{\partial^2 Z}{\partial y^2},$$

and substituting $Z=\phi e^{i(pt+\psi)}$, ϕ and ψ being real functions of x and y, this equation splits up into the two real equations,

$$\frac{1}{\phi}\left\{\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}\right\}-\frac{1}{\mu\phi}\frac{\partial\mu}{\partial x}\frac{\partial\phi}{\partial x}$$
$$-\left\{\left(\frac{\partial\psi}{\partial x}\right)^2+\left(\frac{\partial\psi}{\partial y}\right)^2-p^2\mu\epsilon\right\}=0,\quad.\quad(2)$$

$$\frac{\partial}{\partial x}\left(\phi^2\frac{\partial\psi}{\partial x}\right)+\frac{\partial}{\partial y}\left(\phi^2\frac{\partial\psi}{\partial y}\right)-\frac{1}{\mu}\phi^2\frac{\partial\mu}{\partial x}\frac{\partial\psi}{\partial x}=0.\quad.\quad(3)$$

When ϕ and ψ have been found, determining Z, α and β can be obtained from the equation (1), viz.

$$\alpha=-\frac{1}{\mu}\int\frac{\partial Z}{\partial y}dt$$

$$=-\frac{1}{p\mu}\left(\phi\frac{\partial\psi}{\partial y}-i\frac{\partial\phi}{\partial y}\right)e^{i(pt+\psi)}$$

$$\beta=\frac{1}{p\mu}\left(\phi\frac{\partial\psi}{\partial x}-i\frac{\partial\phi}{\partial x}\right)e^{i(pt+\psi)},$$

and the field is defined by the real vector-components,

$$\left.\begin{aligned} Z&=\phi\cos\theta\\ \alpha&=a\cos(\theta-\xi)\\ \beta&=b\cos(\theta-\eta)\end{aligned}\right\},\quad\ldots\ldots\ldots\ldots\quad(4)$$

where
$$\left.\begin{aligned} a&=-\frac{1}{p\mu}\left\{\phi^2\left(\frac{\partial\psi}{\partial y}\right)^2+\left(\frac{\partial\phi}{\partial y}\right)^2\right\}^{1/2} \\ b&=\frac{1}{p\mu}\left\{\phi^2\left(\frac{\partial\psi}{\partial x}\right)^2+\left(\frac{\partial\phi}{\partial x}\right)^2\right\}^{1/2}\end{aligned}\right\}, \quad . \quad . \quad (5)$$

$$\left.\begin{aligned} \xi&=\tan^{-1}\left\{\frac{\partial\phi}{\partial y}\Big/\phi\frac{\partial\psi}{\partial y}\right\} \\ \eta&=\tan^{-1}\left\{\frac{\partial\phi}{\partial x}\Big/\phi\frac{\partial\psi}{\partial x}\right\}\end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\theta=pt+\psi.$$

The physical interpretation of this result is that the gradual variation of the dielectric causes the magnetic force to get out of step with the electric force; but it should be noted that this effect is not accumulative, and depends, at any point, only on the local variation at that point.

Further, the magnetic force is slightly curved, as is evident from the difference in the time-lags ξ and η; in fact, the wave ceases to be plane.

In what follows, we shall take the variation of the dielectric to be "slow," as compared with the wave-length, so that the amplitude ϕ is practically constant over a considerable range. It would appear that only in this case are we justified in speaking of a "wave" as represented by the function $\phi e^{i(pt+\psi)}$. The magnetic and electric forces will now be practically at right angles, swinging in the wave-fronts of constant phase $\psi=$const., and the direction-cosines of the wave-normal at any point will be proportional to $\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y}$ respectively. An approximate solution of this problem has been discussed elsewhere *.

Evaluating the radiation-flux, according to Poynting, taking the time-average over a complete period, we get

$$\begin{aligned} \mathrm{P}&=\frac{c}{4\pi}\cdot\frac{1}{2\pi}\int_0^{2\pi}(-Z\beta)\,dt \\ &=-\frac{c}{4\pi}\cdot\frac{1}{2\pi}\int_0^{2\pi}\phi\cos(pt+\psi)\cdot\frac{1}{p\mu}\left\{\phi\frac{\partial\psi}{\partial x}\cos(pt+\psi)\right. \\ &\qquad\qquad\left.+\frac{\partial\phi}{\partial x}\sin(pt+\psi)\right\}dt \\ &=-\frac{c}{8\pi p^2\mu}\phi^2\frac{\partial\psi}{\partial x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)\end{aligned}$$

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* Proc. Camb. Phil. Soc. xxii. pt. 2, pp. 124–131 (1924).

$$Q=\frac{c}{4\pi}\cdot\frac{1}{2\pi}\int_0^{2\pi}Z\alpha\,dt$$

$$=-\frac{c}{8\pi p^2\mu}\phi^2\frac{\partial\psi}{\partial y}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

It is seen that the radiation is propagated along the wave-normal, as in a homogeneous medium.

Moreover, we have, on account of equation (3),

$$\frac{\partial P}{\partial x}+\frac{\partial Q}{\partial y}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

in accordance with the non-absorbing character of the medium, and this result is not dependent on the slow variation of quality.

It should also be noted, that in the case of normal incidence, which is most important from our point of view, the equations contain only one variable, x, and there is complete symmetry around the ray, which is then strictly normal to the plane in which the electric and magnetic forces are swinging at right angles to one another. The time-lag between the vectors will, however, persist.

In case of polarization in the xz-plane, the fundamental equations become

$$\epsilon\frac{\partial X}{\partial t}=\frac{\partial\gamma}{\partial y}$$

$$\epsilon\frac{\partial Y}{\partial t}=-\frac{\partial\gamma}{\partial x}$$

$$-\mu\frac{\partial\gamma}{\partial t}=\frac{\partial Y}{\partial x}-\frac{\partial X}{\partial y},$$

which are seen to be completely analogous to the equations (1), leading to similar results.

XVI. *On Orographic Precipitation.* *By* SUMINOSUKE ONO [*].

§ 1. *Introduction.*

IT is a well-known fact in meteorology that the amount of precipitation depends on orographic conditions. We have many reports in which statistics show that the amount of precipitation increases with altitude in the mountain region near a sea-coast. The point of maximum precipitation, however, is not the summit of the mountain. The small rainfall of the basins of Bohemia and Hungary surrounded by the enclosing mountains of Germany and Austria, on which the rainfall is comparatively heavy, is a well-known fact. In Japan, the province of Shinano is also a region of small precipitation surrounded by mountains with somewhat heavier precipitation. These phenomena show evidently that orographic precipitation decreases extremely behind a mountain. A theoretical explanation of these phenomena has been given by Prof. F. Pockels [†]. His calculation shows that under certain assumptions the amount of precipitation increases with the altitude of the land, tending to a maximum at the point at which the inclination is a maximum, and vanishing at the summit of the mountain. This solution must of course be only a first approximation. In the present paper a more general solution, which can be applied to the region behind the mountain, is given; the numerical comparison being taken with the observed values of snow in Yamagata province, which lies in the north-eastern part of Honshu in the Japanese Islands.

§ 2. *Stream Function.*

Though the actual cause of meteorological precipitation may be very complicated, there is no doubt that the precipitation is directly related to the vertical currents of the atmosphere. The real motion of atmospheric air is actually very complicated; it is not steady; it whirls everywhere under the action of viscosity; but our observed data are actually statistical, and the theoretical results which are calculated under very simplified conditions may illustrate many phenomena in the atmosphere satisfactorily.

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[*] Communicated by Sir Napier Shaw, F.R.S. This paper will be submitted to the publishing committee of papers to be dedicated to Professor Nagaoka to commemorate the twenty-fifth anniversary of his professorship.

[†] Pockels, *Ann. d. Physik*, (4) iv. pp. 459-480 (1901).

As is generally done, I shall now assume the current of air to be steady and continuous, free from whirls and friction, and, moreover, all conditions to be two-dimensional, *i. e.* the current is assumed to flow everywhere parallel to a definite vertical plane.

If we designate by x and z the horizontal and vertical coordinates respectively, and by ϕ the velocity potential, which may exist in consequence of the conditions assumed above, then the horizontal and the vertical components of the velocity u and v are

$$u=\frac{\partial\phi}{\partial x},\qquad v=\frac{\partial\phi}{\partial z}.$$

As is well known, the hydrodynamical equation follows

$$\frac{\partial(\rho u)}{\partial x}+\frac{\partial(\rho v)}{\partial x}=0,$$

or

$$\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial z^2}+\frac{1}{\rho}\frac{\partial\rho}{\partial x}\frac{\partial\phi}{\partial x}+\frac{1}{\rho}\frac{\partial\rho}{\partial z}\frac{\partial\phi}{\partial z}=0, \quad . \quad . \quad (1)$$

in which ρ is the density of air.

In this equation the term $\frac{\partial\rho}{\partial x}$ may be assumed to be zero, and $\frac{\partial\rho}{\partial z}$ takes various functional forms corresponding with the assumed conditions. In this paper the following four cases are discussed, but in every case, terms of density variation due to the hydrodynamical effect are neglected.

Case A.—Constant density.

This case is applicable when the consideration is restricted to a comparatively small vertical height.

Since in this case $\frac{\partial\rho}{\partial z}=0$, we have

$$\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial z^2}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The solution of this partial differential equation is

$$\sum_j\{\phi_j(x+iz)+\phi_j(x-iz)\}=0, \quad . \quad . \quad . \quad (3)$$

ϕ_j being an arbitrary function of a complex variable. In many practical cases it will be convenient for calculation if trigonometrical and exponential functions are used.

Case B.—Isothermal.

In this case, by Boyle's law, the density of air is directly proportional to the pressure, and the relation between the pressure p and the vertical coordinate z is given by a logarithmic relation, *viz.*,

$$\log\frac{p_0}{p} = \log\frac{\rho_0}{\rho} = q_1 z.$$

In this equation q_1 is $\frac{g}{\mathrm{RT}}$; g, R, and T denoting the acceleration due to gravity, the gas constant, and the absolute temperature of air respectively. Consequently

$$\frac{1}{\rho}\frac{\partial \rho}{\partial z} = -q_1$$

is a constant, and the equation (1) becomes

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2} - q_1 \frac{\partial \phi}{\partial z} = 0. \quad . \quad . \quad . \quad . \quad (4)$$

Pockels * gave a particular solution of this equation with a series containing trigonometrical terms which may correspond with Fourier's series representing an arbitrary orographic form. But we may have a more general solution of this equation as follows:—

Changing the coordinates x, z into the cylindrical coordinates r, θ (*i. e.*, $x = r\cos\theta$, $z = r\sin\theta$) and substituting $e^{\frac{1}{2}q_1 z + ni\theta}\mathrm{K}(r)$ for ϕ in the last equation, we may have

$$\frac{\partial^2 \mathrm{K}}{\partial r^2} + \frac{1}{r}\frac{\partial \mathrm{K}}{\partial r} - \left\{\left(\frac{q_1}{2}\right)^2 + \frac{n^2}{r^2}\right\}\mathrm{K} = 0. \quad . \quad . \quad (5)$$

Since this equation is satisfied with the cylindrical function of imaginary argument, we have the solution of equation (4)

$$\phi = \mathrm{G}(z) \,.\, x + e^{\frac{1}{2}q_1 z}\sum_j\sum_n (\mathrm{A}_{nj}\cos n\theta_j + \mathrm{B}_{nj}\sin n\theta_j)\mathrm{K}_n(\tfrac{1}{2}q_1 r_j i), \quad . \quad . \quad . \quad (6)$$

in which $\mathrm{K}_n(\frac{1}{2}q_1 r_j i)$ denotes the cylindrical function, and

$$\mathrm{G}(z) \,.\, x = \left\{a + \frac{c}{q_1}e^{q_1 z}\right\} x$$

is a particular solution, a, c, A_{nj}, and B_{nj} being constants.

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* Pockels, *loc. cit.*

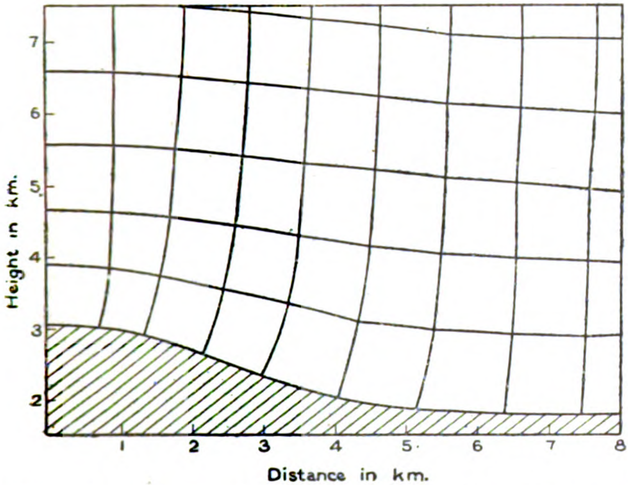
An example of equipotential surfaces and stream lines calculated by this formula is shown in fig. 1, in which the following values of the constants are used :—

$$a = 0{\cdot}01 \text{ km./sec.}, \qquad A_1 = -0{\cdot}001 \text{ km.}^2\text{/sec.},$$

$q_1 = 0{\cdot}125$/km., and all other constants vanish ; *viz.*

$$\phi = ax + Ae^{\frac{1}{2}q_1 z} \cos\theta\, K_1(\tfrac{1}{2}q_1 ri).$$

Fig. 1.



Equipotential surfaces and stream lines in an isothermal distribution.

Case C.—Adiabatic equilibrium.

In this case we have

$$\frac{p}{\rho} = \mathrm{RT}, \qquad \frac{1}{p}\frac{\partial p}{\partial z} = -\frac{g}{\mathrm{RT}}$$

and

$$\frac{1}{p}\frac{\partial p}{\partial z} - \frac{1}{\rho}\frac{\partial \rho}{\partial z} = \frac{1}{\mathrm{T}}\frac{\partial \mathrm{T}}{\partial z} = -\frac{1}{\mathrm{T}}\frac{g}{\mathrm{JC}_p},$$

in which J and C_p denote the mechanical equivalent of heat and the specific heat of air under constant pressure respectively, the other symbols being the same as those used in the former cases.

In virtue of the last equation, we have

$$T = T_0 - \frac{g}{C_pJ} z = T_0(1-\kappa z), \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which T_0 is the temperature at the point $z=0$, and $\frac{g}{JC_pT_0}$ is designated by κ. Consequently we have

$$\frac{1}{\rho}\frac{\partial\rho}{\partial z} = -\frac{g}{RT} + \frac{g}{JC_p}\frac{1}{T}$$

$$= -(q_1-\kappa)\frac{1}{1-\kappa z},$$

$\frac{g}{RT_0}$ being designated by q_1. And equation (1) becomes

$$\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial z^2} - (q_1-\kappa)\frac{1}{1-\kappa z}\frac{\partial\phi}{\partial z} = 0. \quad . \quad . \quad (8)$$

The solution of this equation may be considered as a special case, which is discussed in the next paragraph.

Case D.—Pseudoadiabatic equilibrium.

This is a case where a special state of equilibrium holds, water or ice precipitating steadily in the air. In this case the relation between the temperature and the height is[*]

$$\frac{\partial T}{\partial z} = -\frac{g\left(\frac{1}{J} + \frac{s\omega}{RT}\right)}{C_p + s\omega\frac{1}{b}\frac{\partial b}{\partial T}}. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The notation in this equation is the same as in the former cases, except s, b, and ω, by which the latent heat of vaporization (from liquid phase or solid phase), the saturated vapour-pressure, and the mass of the saturated water vapour in the unit mass of air are designated respectively. And in these ω is given by the following formula,

$$\omega = 0{\cdot}622\,\frac{b}{p},$$

in which 0·622 is the ratio of the molecular weight of water vapour to that of air. Practically s in the above equation may be considered as a constant, while b is a function of the temperature. There are many formulæ by which the relation between the vapour-pressure and the temperature is expressed. But among them is Regnault's formula *, which has been checked by various authors with their measurements, *viz.*:

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[*] Humphreys, 'Physics of the Air,' p. 34 (1920).

$$\log b = c + c'\beta^t + c''\gamma^t ;$$

c, c', c'', β, and γ are constants, and t is the temperature. Since among these β and γ are very near to unity, expanding β^t and γ^t in a series of ascending powers of t and neglecting terms of higher order than the first, the logarithmic value of b can be expressed by a linear function of t, *viz.*:

$$\log b = c + c' + c'' + \{c'(\beta - 1) + c''(\gamma - 1)\}t.$$

Or, designating the value of $\{c'(\beta - 1) + c''(\gamma - 1)\}$ by l, we may write

$$b = b_0 e^{l(\mathrm{T}-\mathrm{T}_0)},$$

where T is the absolute temperature, and b_0 denotes the value of b when T is equal to T_0, the temperature at the point $z=0$.

For the value of p, since $\frac{1}{p}\frac{\partial p}{\partial z} = -\frac{g}{\mathrm{RT}}$, we have

$$p = p_0 e^{-\int_0^z \frac{g}{\mathrm{RT}} dz}.$$

And the equation (9) becomes

$$\frac{\partial \mathrm{T}}{\partial z} = -\frac{g\left\{\frac{1}{\mathrm{J}} + \frac{0{\cdot}622\, s b_0}{\mathrm{RT}\, p_0} e^{l(\mathrm{T}-\mathrm{T}_0) + \int_0^z \frac{g}{\mathrm{RT}} dz}\right\}}{\mathrm{C}_p + 0{\cdot}622 \frac{s b_0 l}{p_0} e^{l(\mathrm{T}-\mathrm{T}_0) + \int_0^z \frac{g}{\mathrm{RT}} dz}} \quad . \quad . \quad (9')$$

But since $\frac{s\omega}{\mathrm{RT}}$ and $s\omega l$ are small compared with $\frac{1}{\mathrm{J}}$ and C_p respectively, it is evident that the first approximate solution must be given in the form

$$\mathrm{T} = \mathrm{T}_0(1 - \kappa' z),$$

where

$$\kappa' = \frac{\frac{g}{\mathrm{T}_0}\left\{\frac{1}{\mathrm{J}} + \frac{0{\cdot}622\, s b_0}{\mathrm{RT}\, p_0} e^{l(\mathrm{T}_1-\mathrm{T}_0) + \int_0^{z_1} \frac{g}{\mathrm{RT}_1} dz}\right\}}{\mathrm{C}_p + 0{\cdot}622 \frac{s b_0 l}{p_0} e^{l(\mathrm{T}_1-\mathrm{T}_0) + \int_0^{z_1} \frac{g}{\mathrm{RT}_1} dz}}$$

T_1 and z_1 being the mean temperature and the mean height respectively. To obtain a more approximate solution, if we put $T_0(1-\kappa' z)$ for T in the right-hand side of the equation (9′), there results

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* Regnault, *Rél. des exp.*

$$T = T_0 - \int_0^z \frac{g\left\{\dfrac{1}{J} + \dfrac{0{\cdot}622\, sb_0}{RT_0\, p_0} e^{lT_0\kappa' z}(1-\kappa' z)^{-1-\frac{g}{RT_0\kappa'}}\right\}}{C_p + 0{\cdot}622\,\dfrac{sb_0 l}{p_0} e^{lT_0\kappa' z}(1-\kappa' z)^{-\frac{g}{RT_0\kappa'}}}\, dz, \quad . \; . \; . \quad (10)$$

and this may be expressed in a power series of z,

$$T = T_0(1-\kappa' z+\kappa'' z^2+\ldots). \quad . \; . \; . \; . \quad (10')$$

On the other hand,

$$-\frac{1}{\rho}\frac{\partial \rho}{\partial z} = -\frac{1}{p}\frac{\partial p}{\partial z} + \frac{1}{T}\frac{\partial T}{\partial z}$$

$$= \frac{1}{T}\left\{\frac{g}{R} + \frac{\partial T}{\partial z}\right\}$$

$$= \frac{\dfrac{g}{RT_0} - \kappa' + 2\kappa'' z + \ldots}{1-\kappa' z+\kappa'' z^2 + \ldots},$$

$$= Q(z), \quad \text{say.}$$

And we have

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2} - Q(z)\frac{\partial p}{\partial z} = 0. \quad . \; . \; . \; . \quad (11)$$

Or, if we neglect the terms of higher order and put

$$\frac{g}{RT_0} - \kappa' = q',$$

it follows that

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2} - \frac{q'}{1-\kappa' z}\frac{\partial \phi}{\partial z} = 0. \quad . \; . \; . \; . \quad (11')$$

This equation is quite similar to equation (8) in the case of the adiabatic equilibrium.

To solve this equation, if we put

$$\phi = (1-\kappa' z)^{-\frac{q'}{2\kappa'}}\psi,$$

we have

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial z^2} - \left(\frac{q'^2}{4} - \frac{q'\kappa'}{2}\right)\frac{\psi}{(1-\kappa' z)^2} = 0.$$

In this equation, since κ' is very small, we can put

$$\frac{1}{(1-\kappa' z)^2} = e^{2\kappa' z},$$

and denoting the value $\frac{q'^2}{4} - \frac{q'\kappa'}{2}$ by $\frac{1}{4}q^2$,

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial z^2} - \frac{q^2}{4} e^{2\kappa' z}\psi = 0.$$

Now changing the variables x, z to x', z', which are defined by the following equations:

$$\left.\begin{aligned} z' + ix' &= \frac{1}{\kappa'}\left\{e^{\kappa'(z+ix)} - 1\right\} \\ z' - ix' &= \frac{1}{\kappa'}\left\{e^{\kappa'(z-ix)} - 1\right\} \end{aligned}\right\}, \quad . \quad . \quad . \quad (12)$$

the equation (11′) becomes

$$\frac{\partial^2\psi}{\partial x'^2} + \frac{\partial^2\psi}{\partial z'^2} - \frac{q^2}{4}\psi = 0,$$

which is quite similar to equation (4). Thus the solution of equation (11′) must be

$$\phi = G(z) \, . \, x$$
$$+ (1-\kappa' z)^{-\frac{q'}{2\kappa'}} \sum_j \sum_n (A_{nj}\cos n\theta_j' + B_{nj}\sin n\theta_j') K_n\left(\frac{q}{2} r_j' i\right), \quad . \quad . \quad . \quad (13)$$

where

$$G(z) = a + c\int^z e^{\int^z \frac{q'}{1-\kappa' z}dz} dz = a + \frac{c}{q' - \kappa'}(1-\kappa' z)^{-\frac{q'}{\kappa'}+1},$$

$$r'^2 = x'^2 + z'^2 = \frac{1}{\kappa'^2}\left\{e^{2\kappa' z} - e^{\kappa'(z+ix)} - e^{\kappa'(z-ix)} + 1\right\},$$

$$\theta' = \frac{1}{i}\log\frac{z'+ix'}{r'},$$

z' and x' being defined by equations (12).

But this solution is rather impractical; a more practical one (though it is a particular solution) is as follows:—

Equations (2), (4), (8), and (11) can be written in the form

$$\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial z^2} - Q(z)\frac{\partial\phi}{\partial z} = 0, \quad . \quad . \quad . \quad (14)$$

where $Q(z)$ is a function of z representing the value of

$-\frac{1}{\rho}\frac{\partial\rho}{\partial z}$, and it is evident that the function $Q(z)$ can be expressed as a power series of z,

$$Q(z) = q(1+\kappa_1 z+\kappa_2 z^2+\ \ldots).$$

Thus if we put

$$\phi = e^{\frac{1}{2}\int^z Q(z)\,dz+F(x,z)},$$

this satisfies equation (14) when the constants α_s, α_s' and ϵ, ϵ' in the following expression for $F(x,z)$ are suitable.

$$F(x,z) = \alpha_0+\alpha_{1\cdot 0}x+\alpha_{1\cdot 1}z+\alpha_{2\cdot 0}x^2+\alpha_{2\cdot 1}xz+\alpha_{2\cdot 2}z^2+\ \ldots$$

$$+\epsilon\log x+\epsilon'\log z+\frac{\alpha'_{1\cdot 0}}{x}+\frac{\alpha'_{1\cdot 1}}{z}+\ \ldots. \quad . \quad . \quad (15)$$

Or more simply, if we put

$$F(x,z) = \epsilon\log x+\epsilon'\log z+\alpha_0+\alpha x+\beta z+\beta' z^2+\ \ldots, \quad (15')$$

as the condition for satisfying equation (15′), there follows

$$\epsilon^2-\epsilon = 0, \qquad \epsilon'^2-\epsilon' = 0,$$

$$\alpha\epsilon = 0, \qquad \beta\epsilon' = 0,$$

$$\alpha^2+\beta^2+2\beta'+4\beta'\epsilon' = \tfrac{1}{4}q^2-\tfrac{1}{2}q\kappa_1,$$

$$4\beta\beta'+6\beta''+6\beta''\epsilon' = \tfrac{1}{2}q^2\kappa_1-q\kappa_2,$$

$$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot$$

Of these the first four equations are satisfied by the following four sets of values :—

(i.) $\epsilon = 1, \quad \epsilon' = 0, \quad \alpha = 0,$

(ii.) $\epsilon = \epsilon' = 1, \quad \alpha = \beta = 0,$

(iii.) $\epsilon = 0, \quad \epsilon' = 1, \quad \beta = 0,$

(iv.) $\epsilon = \epsilon' = 0.$

It is evident that the first two sets of these correspond to the particular solution

$$G(z)x = \left\{a+c\int^z e^{\int^z Q(z)\,dz}\,dz\right\}x,$$

and the others become the solution which may be written in a form $e^{\alpha x+\beta z}E(z)$, $E(z)$ being a function of z only. Here we can take, for convenience' sake, $\alpha^2+\beta^2=\frac{1}{4}q^2$. And the solution for ϕ becomes

$$\phi = \left\{a+c\int^z e^{\int^z Q(z)\,dz}\,dz\right\}x+e^{\frac{1}{2}\int^z Q(z)\,dz}\sum_j e^{\alpha_j x+\beta_j z}E_j(z).$$

$$. \quad . \quad . \quad (16)$$

As a special case of this solution, if we put $Q(z)=q$ (a constant), $E_j(z)$ becomes constant. Designating this constant by A_j, it follows,

$$\phi = \left(a + \frac{c}{q} e^{qz}\right) x + \sum_j A_j e^{\alpha_j x + (\beta_j + \frac{1}{2}q) z} . \quad . \quad . \quad (16')$$

Or more practically, if we express α_j and β_j in the form of a complex number

$$\alpha_j = \lambda_j + m_j i,$$

$$\beta_j + \tfrac{1}{2}q = \mu_j + n_j i,$$

taking $\alpha_j^2 + \beta_j^2 = \frac{1}{4}q^2$, it follows that

$$m_j^2 - \lambda_j^2 + n_j^2 - \mu_j^2 + \mu_j q = 0,$$

$$2m_j\lambda_j + 2n_j\mu_j - n_j q = 0.$$

And the stream function becomes

$$\phi = \left(a + \frac{c}{q} e^{qz}\right) x + \sum_j A_j \cos(m_j x + n_j z + \theta_j)\, e^{\lambda_j x + \mu_j z}, \quad (16'')$$

in which a, c, A_j, and θ_j are arbitrary constants. Pockel's solution is a special case of this. In his solution, the constant μ_j in this equation is restricted to be negative. But it seems to be rather natural if it is taken as a positive constant. An example of the recent observations in Japan is shown in Table I. The figures are the mean of 14 observations which were made by Mr. S. Sekine in 1921 and 1922, by the method of pilot balloons, at the Tokorozawa Military Meteorological Station, where the orographic effects, if any,

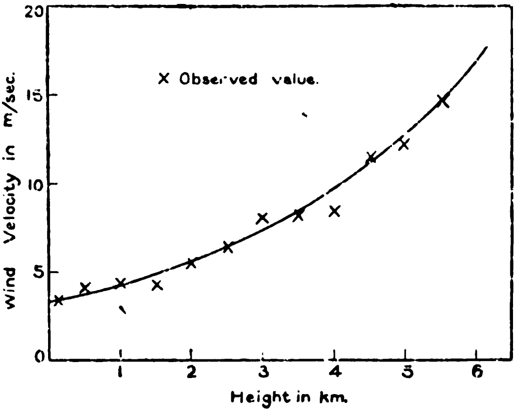
TABLE I.

Height.	Horizontal Wind Velocity.	Height.	Horizontal Wind Velocity.
km.	m./sec.	km.	m./sec.
0·1	3·3	3·0	8·0
0·5	4·1	3·5	8·2
1·0	4·4	4·0	8·4
1·5	4·3	4·5	11·4
2·0	5·5	5·0	12·2
2·5	6·7	5·5	14·7

are considered to be very small. In fig. 2 this relation between the horizontal velocity and the height is shown graphically. By these we can see that the horizontal velocity u can be given by a simple exponential function. The curve in this figure represents the value calculated by a formula $Ae^{\mu z}$, the values of the constants being

$$A = 3{\cdot}27 \text{ m./sec.} \quad \text{and} \quad \mu = +0{\cdot}274/\text{km.}$$

Fig. 2.



Relation between wind velocity and height at Tokorozawa deduced from observations of pilot balloons.

§ 3. *Equation for Stream Lines.*

The constants in the above formulæ for the stream function, solved in the last paragraph, must be determined by the boundary conditions. For the purpose of determining these constants, we must have the equation for the stream line. If we denote this equation in a form $\chi=0$, the function χ must be given by the relation

$$\frac{\partial\phi}{\partial x}\frac{\partial\chi}{\partial x}+\frac{\partial\phi}{\partial z}\frac{\partial\chi}{\partial z}=0.$$

When the stream function ϕ is defined by equation (14),

$$\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial z^2}-Q(z)\frac{\partial\phi}{\partial z}=0,$$

it is easily shown that the function χ must be given in the following form :

$$\chi = \int^{x} \frac{\partial \phi_1}{\partial z} \partial x + G'(z)\frac{x^2}{2} - e^{\int^{z} Q(z)\,dz} \int^{z} G(z)\, e^{-\int^{z} Q(z)\,dz} dz + N e^{\int^{z} Q(z)\,dz}, \quad . \quad (17)^*$$

in which N is the constant of integration and $G'(z)$ is $\frac{d}{dz}(G(z))$, and ϕ_1 is $\phi - G(z)x$.

---

* The lower limit of the integration in the first term of this equation is omitted. If we take this limit of the integration as $x=\gamma$, and express the first term as $\int_{\gamma}^{x} \frac{\partial \phi_1}{\partial z} \partial x$, this is equivalent to the addition of a term $\left[\int \frac{\partial \phi_1}{\partial z} \partial z\right]_{x=\gamma}$, which is a function of z only. But in this case it is evident that another term,

$$-e^{+\int^{z} Q(z)\,dz} \int^{z} \left(\frac{\partial \phi_1}{\partial x}\right)_{x=\gamma} e^{-\int^{z} Q(z)\,dz} dz, \quad . \quad . \quad . \quad (A)$$

must be added at the same time, for the sake of satisfying the necessary condition which is given by equation (14).

If we put now

$$Z = \int_{\gamma} \frac{\partial \phi_1}{\partial z} \partial x,$$

since

$$\frac{\partial^2 \phi_1}{\partial x^2} + \frac{\partial^2 \phi_1}{\partial z^2} - Q(z)\frac{\partial \phi_1}{\partial z} = 0,$$

we have

$$Z = -\int^{z} \partial z \int^{\gamma} \frac{\partial^2 \phi_1}{\partial z^2} \partial x = \int^{z} \partial z \int^{\gamma} \left\{ \frac{\partial^2 \phi_1}{\partial x^2} - Q(z)\frac{\partial \phi_1}{\partial z} \right\} \partial x,$$

$$= \int^{z} \partial z \left[\left(\frac{\partial \phi_1}{\partial x}\right)_{x=\gamma} - Q(z) \int^{\gamma} \left(\frac{\partial \phi_1}{\partial z}\right) \partial x \right]$$

$$= \int^{z} \partial z \left[\left(\frac{\partial \phi_1}{\partial x}\right)_{x=\gamma} + Q(z)\, Z \right].$$

Solving this equation, we shall find that

$$Z = e^{\int^{z} Q(z)\,dz} \int^{z} \left(\frac{\partial \phi_1}{\partial x}\right)_{x=\gamma} e^{-\int Q(z)\,dz} dz.$$

This is a term which cancels with the term shown in (A).

The following formulæ are solutions for various cases :—

(*a*) If $Q(z) = q$, a constant,

$$\chi = \int^x \left(\frac{\partial \phi_1}{\partial z}\right) \partial x + c\, e^{qz} \frac{x^2}{2} - \frac{c}{q} z\, e^{qz} + \frac{a}{q} + \mathrm{N}\, e^{qz} = 0. \quad . \quad . \quad . \quad (18)$$

(*b*) If

$$\phi = \mathrm{A} \cos\theta\, \mathrm{K}_1^{(1)}\left(\frac{q}{2} ri\right) e^{\frac{q}{2} z} + ax,$$

$$\chi = \mathrm{A} \sin\theta\, \mathrm{K}_1^{(1)}\left(\frac{q}{2} ri\right) e^{\frac{q}{2} z} + i\, \mathrm{K}_0^{(1)}\left(\frac{q}{2} ri\right) e^{\frac{q}{2} z} + \frac{a}{q} + \mathrm{N}\, e^{qz} = 0. \quad (19)$$

If

$$\phi = \sum_j \mathrm{A}_j \cos\theta_j\, \mathrm{K}_1^{(1)}\left(\frac{q}{2} r_j i\right) e^{\frac{q}{2} z} + ax,$$

$$\chi = \sum_j \left\{ \mathrm{A}_j \sin\theta_j\, \mathrm{K}_1^{(1)}\left(\frac{q}{2} r_j i\right) + i\, \mathrm{K}_0^{(1)}\left(\frac{q}{2} r_j i\right) \right\} e^{\frac{q}{2} z} + \frac{a}{q} + \mathrm{N}\, e^{qz} = 0. \quad (19')$$

(*c*) If

$$\phi = \mathrm{G}(z) \,.\, x + \sum_j e^{\alpha_j x + \beta_j z}\, \mathrm{E}_j(z),$$

$$\chi = \sum_j e^{\alpha_j x + \beta_j z} \left\{ \frac{\beta_j}{\alpha_j} \mathrm{E}_j(z) + \frac{1}{\alpha_j} \mathrm{E}'(z) \right\} + \mathrm{G}'(z) \frac{x^2}{2} - e^{\int^z \mathrm{Q}(z)\, dz} \int^z \mathrm{G}(z)\, e^{-\int^z \mathrm{Q}(z)\, dz}\, dz + \mathrm{N}\, e^{\int^z \mathrm{Q}(z)\, dz} = 0. \quad (20)$$

If

$$\phi = ax + \sum_j \mathrm{A}_j \cos(m_j x + n_j z + \theta_j)\, e^{\lambda_j x + \mu_j z},$$

$$\chi = \sum_j \mathrm{A}_j \left[\frac{m_j n_j + \lambda_j \mu_j}{m_j^2 + \lambda_j^2} \cos(m_j x + n_j z + \theta_j) - \frac{n_j \lambda_j - m_j \mu_j}{m_j^2 + \lambda_j^2} \sin(m_j x + n_j z + \theta_j) \right] e^{\lambda_j x + \mu_j z} + \frac{a}{q} + \mathrm{N}\, e^{qz} = 0. \quad (21)$$

In this equation, if we put

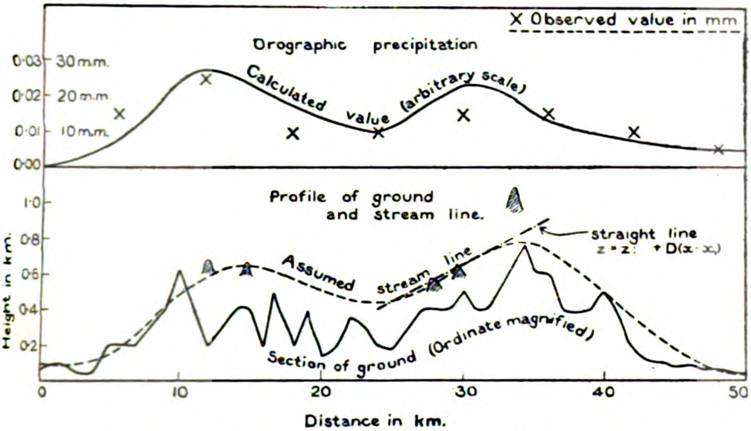
$$\mathrm{A}_j \frac{m_j n_j + \lambda_j \mu_j}{m_j^2 + \lambda_j^2} = \mathrm{C}_j \cos\alpha_j, \qquad \mathrm{A}_j \frac{n_j \lambda_j - m_j \mu_j}{m_j^2 + \lambda_j^2} = \mathrm{C}_j \sin\alpha_j,$$

we can write

$$\chi = \sum_j \mathrm{C}_j \cos(m_j x + n_j z + \theta_j + \alpha_j) + \frac{a}{q} + \mathrm{N}\, e^{qz} = 0. \quad . \quad . \quad . \quad (21')$$

The dotted curve in fig. 3 is an example of the last equation representing the smoothed form of the assumed stream line, approximating to the actual profile of the ground of a local part in Yamagata Province. (The ordinate in this figure is magnified to exaggerate the irregularities of the form.) The actual section of the ground cut by a vertical plane in the direction N.W.–S.E. is shown with a full line. And the shaded forms of summits show the situation of mountains which are very near to the section.

Fig. 3.



In the case of such application it is sufficient if we take two special cases: *i. e.*,

(i.) $n_j = 0, \quad \lambda_j = 0, \quad$ and $\quad \alpha_j + \theta_j = 0.$

(ii.) $m_j = 0 \quad$ and $\quad \alpha_j + \theta_j = 0.$

And for the profile of the ground, since the value of z, which represents the height of the ground, is very small compared with the other distances, we may have

$$\sin n_j z = n_j z, \quad \cos n_j z = 1, \quad e^{\mu_j z} = 1 + \mu_j z, \quad \text{and} \quad e^{qz} = 1 + qz.$$

Consequently

$$z = \frac{-\left(\frac{a}{\mathrm{N}q} + 1\right)\frac{1}{q} - \sum\limits_{n=0,\,\lambda=0} \frac{\mathrm{C}_j}{\mathrm{N}q} \cos m_j x - \sum\limits_{m=0} \frac{\mathrm{C}_j}{\mathrm{N}q} e^{\lambda_j x}}{1 + \sum\limits_{n=0,\,\lambda=0} \frac{\mathrm{C}_j}{\mathrm{N}q} \mu_j \cos m_j x + \sum\limits_{m=0} \frac{\mathrm{C}_j}{\mathrm{N}q} \mu_j e^{\lambda_j x}}. \quad (22)$$

By such simplification the constants are easily determined. The values in the present example are

TABLE II.

j.	$\dfrac{C_j}{Nq}$.	m_j.	n_j.	$\alpha_j+\theta_j$.	λ_j	μ_j.
1 ...	+0·25	$2\pi/48$	0	0	0	−0·0894
2 ...	+0·25	$2\pi/24$	0	0	0	−0·216
3 ...	+0·70	0	+0·0272	0	−0·0578	+0·051
4 ...	+0·70	0	+0·139	0	−0·148	+0·051

and

$$\tfrac{1}{2}q = \mu_3 = \mu_4 = 0{\cdot}051,$$

$$\left(\frac{a}{Nq}+1\right)\frac{1}{q} = -0{\cdot}60,$$

the unit of length being taken in kilometres.

It must be remarked that the value of N, in these, remains arbitrary.

§ 4. *Amount of Precipitation.*

It is evident that the amount of water or snow precipitated in unit time in the air-current through unit area of a horizontal plane will be given by

$$-\partial(v\omega\rho),$$

in which ρ is the density of air, v the vertical component of the air-current, and ω the amount of water vapour contained in a unit mass of air. Or, if we consider that the precipitation is produced within certain limits of height h_1 and h_2, the amount of the precipitation produced in a vertical column with unit area of the cross-section is

$$-\int_{h_1}^{h_2}\frac{\partial(v\omega\rho)}{\partial h}dh = v_1\omega_1\rho_1 - v_2\omega_2\rho_2, \quad . \quad . \quad (23)$$

in which v_1, ω_1, ρ_1 and v_2, ω_2, ρ_2 are values of v, ω, ρ at $h=h_1$ and $h=h_2$ respectively. Here we may expect that the value of $v_2\omega_2\rho_2$ is very small in most cases, because v_2 must be very small.

Now we have to consider how the precipitation falls through the air, and what is its distribution on the ground. It is evident that the precipitation does not fall vertically, but flows some distance with the air-current, and this distance depends upon the velocity of the air and on the size and the form of the precipitation. But the size and the form of the precipitation are not entirely constant. For the sake of convenience I shall now consider statistically the distribution of flow of the precipitation condensed in a vertical plane perpendicular to the x-axis. A part of the precipitation condensed in a vertical plane $x=x'$ will fall in a plane not far from that plane $x=x'$, but some part will flow to a very distant place. Such a distribution must be considered as a function of x, and in ordinary cases it will have a maximum point for a certain value of x, and must vanish when $x=\infty$. Such a function can be expressed by a series of exponential functions* ; *i. e.*,

$$f(x) = \sum_s \eta_s e^{\eta_s(x-x')},$$

where $x > x'$ and the η_s's are constants. In the present case the maximum point of $f(x)$ can be considered to be very near to the plane $x=x'$, and we may write very approximately $f(x)=\eta e^{-\eta(x-x')}$, and the precipitation at any point will be proportional to

$$W = \int_{x_1}^{x} (v_1\omega_1\rho_1)\eta e^{-\eta(x-x')}\,dx' - \int_{x_1}^{x} (v_2\omega_2\rho_2)\eta e^{-\eta(x-x')}\,dx',$$

x_1 being a certain value of x which shows the limit of the region producing the precipitation.

Thus, if we use the equation (16), *viz.*,

$$\phi = G(z)\,.\,x+\sum_j e^{a_jx+\beta_jz}E_j(z),$$

we have

$$v = \frac{\partial\phi}{\partial z} = G'(z)\,.\,x+\sum_j e^{a_jx+\beta_jz}\{\beta_jE_j(z)-E'_j(z)\};$$

hence

$$\begin{aligned}W = \{G'(z_1)\omega_1\rho_1 - G'(z_2)\omega_2\rho_2\}\Big\{x - x_1e^{-\eta(x-x_1)} - \frac{1}{\eta}(1-e^{-\eta(x-x_1)})\Big\}\\ + \sum_j\Big\{\frac{\eta}{a_j+\eta}\big[(\beta_jE_j(z_1)+E'_j(z_1))\omega_1\rho_1e^{\beta_jz_1}\\ - (\beta_jE_j(z_2)+E'_j(z_2))\,\omega_2\rho_2e^{\beta_jz_2}\big](e^{a_jx}-e^{a\,x_1}e^{-\eta(x-x_1)})\Big\}.\end{aligned} \quad \ldots \quad (24)$$

Or, in the case of equation (16″), we have

$$\phi = \left(a+\frac{c}{q}e^{qz}\right)x+\sum_j A_j\cos(m_jx+n_jz+\theta)\,e^{\lambda_jx+\mu_jz},$$

$$\begin{aligned}v = ce^{qz}\,.\,x+\sum_j A_j\{\mu_j\cos(m_jx+n_jz+\theta_j)\\ -n_j\sin(m_jx+n_jz+\theta_j)\}\,e^{\lambda_jx+\mu_jz}.\end{aligned}$$

---

* Some notes about this are given in the author's other paper (Journ. of Met. Soc. of Japan, 1923, p. 127).

Neglecting $v_2\omega_2\rho_2$,

$$
\begin{aligned}
W = & \; ce^{\eta z_1}\omega_1\rho_1 \left\{ x - x_1 e^{-\eta(x-x_1)} - \frac{1}{\eta}\left(1 - e^{\eta(x-x_1)}\right) \right\} \\
& + \sum_j \frac{A_j\omega_1\rho_1\eta}{m_j^2 + (\lambda_j+\eta)^2} \Big\{ \big[S_j \cos(m_j x + n_j z_1 + \theta_j) \\
& \qquad\qquad + S_j' \sin(m_j x + n_j z_1 + \theta_j) \big] e^{\lambda_j x + \mu_j z_1} \\
& - \big[S_j \cos(m_j x_1 + n_j z_1 + \theta_j) \\
& \qquad + S_j' \sin(m_j x_1 + n_j z_1 + \theta_j) \big] e^{\lambda_j x_1 + \mu_j z_1} e^{-\eta(x-x_1)} \Big\}, \qquad (25)
\end{aligned}
$$

where

$$
\begin{aligned}
S_j &= \mu_j(\lambda_j+\eta) + m_j n_j, \\
S_j' &= \mu_j m_j - n_j(\lambda_j+\eta).
\end{aligned}
$$

Of course this formula is applicable to the region where $\frac{\partial z}{\partial x} > 0$.

When there are many maxima and minima in the curve of the stream line, let $x=x_1$ be the vertical plane in which the air-current begins to ascend, and $x=x_2$ the vertical plane in which the first maximum point of the stream line lies, $x=x_3$ the vertical plane in which the next minimum point lies, $x=x_4$ the vertical plane in which the second maximum point lies, and so on.

Then it is evident that

$$W_1 = \int_{x_1}^{x} (v_1\omega_1\rho_1)\eta\, e^{-\eta(x-x')}\, dx' \qquad \text{for} \quad x_1 < x < x_2,$$

$$W_2 = \int_{x_1}^{x_2} (v_1\omega_1\rho_1)\eta\, e^{-\eta(x-x')}\, dx' = W_1\, e^{-\eta(x-x_2)} \quad \text{for} \quad x_2 < x < x_3,$$

$$W_3 = \int_{x_1}^{x_2} (v_1\omega_1\rho_1)\eta e^{-\eta(x-x')}\, dx' + \int_{x_3}^{x} (v_1\omega_1\rho_1) e^{-\eta(x-x')}\, dx' \qquad \text{for} \quad x_3 < x < x_4,$$

etc.

If the top of the mountain is higher than the lowest limit of the precipitating cloud, the value of z_1 must be considered as a function of x. In this case the integration will be very complicated. But for practical purposes an approximate calculation can be obtained easily. Since the maximum difference of z in a stream line near to the ground is not so great compared with the other length, and terms of higher orders containing z can be neglected, we may have approximately

$$
\begin{aligned}
v_1 = \sum_j A_j \Big\{ & -n_j \sin(m_j x + \theta_j) + \mu_j \cos(m_j + \theta_j) \\
& + \left(-2n_j\mu_j \sin(mj + \theta_j) + (\mu_j^2 - n_j^2)\cos(m_j x + \theta_j)\right) z \Big\} e^{\lambda_j x},
\end{aligned}
$$

and
$$\rho\omega = \rho_0\omega_0\{1-(l\kappa'\mathrm{T}_0-\kappa')z\}$$
$$= \rho_0\omega_0(1-rz) \quad \text{say.}$$

Here, in the expression of r, a term $ce^{qz}.x$ is omitted for the sake of avoiding troublesome complications. Though there is some necessity for this term, it is evident that the integration for this term is very easy.

By such simplification we have

$$r_1\rho_1\omega_1 = \rho_0\omega_0\sum_j \mathrm{A}_j\Big[-n_j\sin(m_jx+\theta_j)+\mu_j\cos(m_jx+\theta_j)$$
$$+\{n_j(r-2\mu_j)\sin(m_jx+\theta_j)$$
$$+(\mu_j^2-\mu_jr-n_j^2)\cos(m_jx+\theta_j)\}z\Big]e^{\lambda_jx}.$$

Moreover, if we assume a short part of a stream line near to the ground as a straight line, represented by the equation

$$z = z_1'+\mathrm{D}(x-x_1),$$

it is evident that this value for z can be used for approximate calculation. An example of such straight line, which is used for numerical calculation in this paper, is shown in fig. 3.

Thus we may have

$$\mathrm{W} = \int_{x_1}^{x}(r_1\rho_1\omega_1)\eta e^{-\eta(x-x')}\,dx'$$
$$= \rho_0\omega_0\sum_j \mathrm{A}_j\eta e^{-\eta x}\int_{x_1}^{x}\{(\mathrm{P}+\mathrm{Q}x')\cos(m_jx'+\theta_j)$$
$$+(\mathrm{P}'+\mathrm{Q}'x')\sin(m_jx'+\theta_j)\}\,e^{(\eta+\lambda)x'}\,dx'$$
$$= \rho_0\omega_0 e^{-\eta x}\sum_j \mathrm{A}_j\eta\Big|\{(\mathrm{L}+x'\mathrm{M})\cos(m_jx'+\theta_j)$$
$$+(\mathrm{L}'+x'\mathrm{M}')\sin(m_jx'+\theta_j)\}\,e^{(\eta+\lambda)x'}\Big|_{x'=x_1}^{x'=x}$$

where . . . (26)

$$\mathrm{P} = \mu_j+(-\mu_jr+\mu_j^2-n_j^2)(z_1'-\mathrm{D}x_1),$$
$$\mathrm{P}' = -n_j+n_j(r-2\mu_j)(z_1'-\mathrm{D}x_1),$$
$$\mathrm{Q} = (-\mu_jr+\mu_j^2-n_j^2)\mathrm{D},$$
$$\mathrm{Q}' = n_j(r-2\mu_j)\mathrm{D},$$

and
$$\mathrm{L} = \frac{(\mathrm{P}-\mathrm{M})(\lambda_j+\eta)-(\mathrm{P}'-\mathrm{M}')m_j}{(\lambda_j+\eta)^2+m_j^2},$$

$$\mathrm{L}' = \frac{(\mathrm{P}-\mathrm{M})m_j+(\mathrm{P}'-\mathrm{M}')(\lambda_j+\eta)}{(\lambda_j+\eta)^2+m_j^2},$$

$$\mathrm{M} = \frac{\mathrm{Q}(\lambda_j+\eta)-\mathrm{Q}'m_j}{(\lambda_j+\eta)^2+m_j^2},$$

$$\mathrm{M}' = \frac{\mathrm{Q}m_j+\mathrm{Q}'(\lambda_j+\eta)}{(\lambda_j+\eta)^2+m_j^2}.$$

As a numerical example, taking the values of the constants given in Table II., the calculated values of W are shown in Table III. The value of η in these is calculated using the observed values which are shown in Table IV. The value of W between $x=12$ km. and $x=24$ km. and between $x=36$ km. and $x=48$ km. can be assumed as a mere function proportional to $e^{-\eta(x-x_1)}$, and we can determine the value of η by the relation

Table III.

x (km.) ……	0	6	12	18	24	30	36	42	48
$\frac{\mathrm{W}}{\mathrm{N}q\rho_0\omega_0}$ ……	0	0·008	0·028	0·017	0·010	0·022	0·013	0·008	0·005

$$\eta = \frac{\log\text{(ratio of orographic precipitation)}}{\text{distance}}.$$

By such method we have values $\eta=0{\cdot}076$/km. between $x=12$ km. and $x=24$ km., and $\eta=0{\cdot}092$/km. between $x=36$ km. and $x=48$ km. The mean of these is $0{\cdot}084$/km. In the present calculation this mean value is used.

The points giving maximum and minimum heights are approximately

Minimum height.	Maximum height.
$x = 0$ km.	$x = 14{\cdot}3$ km.
$x = 23{\cdot}4$,,	$x = 34{\cdot}7$,,

For the calculation between $x=0$ and the second minimum point the formula (25) is used, assuming $z_1=0{\cdot}5$ km. By this assumption $z_1=0{\cdot}5$ km., a little part of the ground becomes higher than this height. But since such part is short, the same formula is assumed to hold good over this range. For the range between the second minimum point and the second maximum point the formula (26) is used, taking values $z_1'=0{\cdot}4$ km. and $\mathrm{D}=0{\cdot}0417$.

The curve representing these values is shown in fig. 3. We can observe that this curve resembles very well the distribution of snow in the mountain region. To compare such values calculated by the formulæ with the actual amount of the precipitation, the amount of snow precipitated on the 20th and the 21st Jan., 1921, is estimated from observations made at several local stations in the vicinity of the region taken in the present example. This precipitation was due to a cyclone which passed through the northern part of Hondo Island from west to east. But the direction of the wind in this locality was N.W. during the time of precipitation. The observed values were plotted on a map, and, drawing the locus of the points of equal precipitation, the amount of the precipitation at the points in the present example was estimated from such locus. Such estimated values are shown in Table IV. The numbers in the row specified as orographic precipitation are the difference between the precipitation at that point and that at $x=0$. These values are also shown graphically in fig. 3.

TABLE IV.

x, in km.	0	6	12	18	24	30	36	42	48
Precipitation, in mm.	15	30	40	25	25	30	30	25	20
Orographic Precipitation, in mm.	0	15	25	10	10	15	15	10	5

We can see that the part of precipitation which is considered as orographic precipitation has fairly good coincidence with the calculated value.

The absolute value must also be calculable from the formula. According to observations at Yamagata meteorological station *, where observations are made every two hours, the total precipitation during January 1921 was 78·2 mm. on 26 occasions, the total duration being 316 hours. The author has proved in another paper † that the mean duration of such phenomena, calculated from the result of the periodic observation, is longer than the true mean value by one period of observation. In this case, since the period of the observation is two hours, the total duration as computed must be considered as longer by 2 × 26 hours than the true duration. Or the true duration will be (316−52)h. = 264 h. Thus the mean precipitation in unit time is

$$\frac{78\cdot2}{264\times3600}\text{ mm./sec.}=0\cdot82\times10^{-4}\text{ mm./sec.}$$

---

* Yamagata station, about 65 km. distant from the origin of present example.

† Ono, *loc. cit.* Journ. of Met. Soc. of Japan, 1923, p. 127.

On the other hand, at the point $x=30$ km. in the former example the amount of the mean precipitation is estimated to be from 5 times to 10 times greater than that at Yamagata. If we assume the value of W at the point $x=30$ km. to be

$$5\times 0{\cdot}82\times 10^{-4}\ \text{mm./sec.} = 4{\cdot}2\times 10^{-5}\ \text{cm./sec.},$$

we must have

$$4{\cdot}2\times 10^{-5}\ \text{gm./cm.}^2\ \text{sec.} = \mathrm{N}q\omega_0\rho_0\times 0{\cdot}022\ \text{gm./cm.}^2\ \text{sec.}$$

In this equation, if we put

$$\omega_0 = 3{\cdot}745\times 10^{-8}\ (\text{at } 0^\circ\text{C.}),$$

$$\rho_0 = 1{\cdot}293\ \text{gm./cm.}^3,$$

then

$$\mathrm{N}q = \frac{4{\cdot}2\times 10^{-5}}{3{\cdot}745\times 1{\cdot}293\times 10^{-6}\times 0{\cdot}022}\ \text{cm./sec.} = 3{\cdot}9\ \text{m./sec.}$$

And since, $$\left(\frac{a}{\mathrm{N}q}+1\right)\frac{1}{q} = -0{\cdot}60,$$

$$a = (1-0{\cdot}60\,q)\mathrm{N}q \doteqdot \mathrm{N}q = 3{\cdot}9\ \text{m./sec.}$$

This shows that such amount of precipitation in this locality can be produced when $\mathrm{N}q=3{\cdot}9$ m./sec., which is approximately proportional to a (the horizontal wind velocity in the flat region). The locality of the present example is one of the most snowy places in Japan. By this calculation it is shown that an amount of snow in this locality can be produced merely as the result of the orographic effect, if there is a wind of 3·9 m./sec., in the mean, during 264 hours in the month of January. Or, since the orographic precipitation is proportional to the value of $\mathrm{N}q$, if the total mean velocity of wind in January is greater than 1·4 m./sec., such an amount of snow can be precipitated in this locality. With this result we can conclude that the snowy climate in the northern localities of Japan is due chiefly to the orographic precipitation.

I wish to express my thanks to Prof. T. Okada, Prof. S. Sano, and Prof. T. Terada for their kind advice and encouragement, and to Messrs. K. Morita, K. Funayama, and S. Sekine for their kindness in having sent me the result of their valuable observations. I am also much obliged to Sir Napier Shaw, who has shown much interest in my work and has kindly introduced my paper in England.

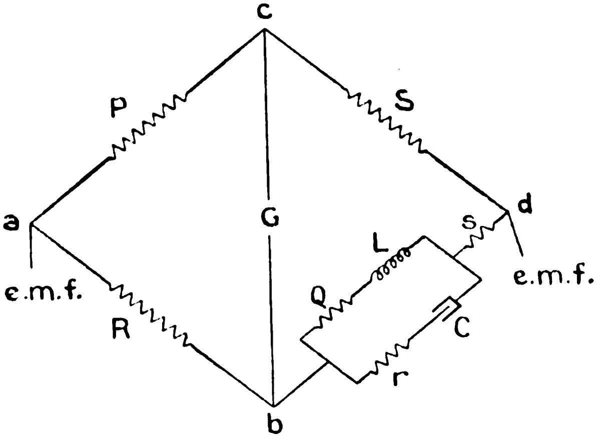
XVII. *On a Method of comparing Inductance and Capacity.*

By Prof. J. M. Ganguli, *M.Sc.*, *Physics Department, Victoria College, Gwalior, India*[*].

A FEW years back Prof. W. E. Forsythe[†], of the University of Wisconsin, U.S.A., gave an interesting and quite a convenient method for comparing "inductance" and "capacity." It was apparently meant to get rid of some of the difficulties in the ordinary bridge methods, and being tried in his laboratory is said to have given good results. In the ordinary bridge methods there being generally two conditions of balance, the one due to steady current and the other due to reactance (the latter being more or less dependent on the first), it is, as the author says, "often difficult to know just what resistance to choose." To quote from him again, "It often happens that with the capacity and inductance to be compared, the first will be so chosen that the second balance cannot be obtained."

In his method he has tried to get over this difficulty by making the two conditions independent. Finding the experiment interesting I tried it under different conditions with different inductances, and observed that though it was more or less satisfactory in some cases it did not work well, especially when the ohmic resistance of the inductance was increased.

The theory, to quote from the author, is this :—



The connexions are shown in the above sketch. P, R, S, Q, *r*, *s*, are non-inductive resistances, L the inductive coil, and C the capacity. a and d are connected to an alternating e.m.f. of frequency n.

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[*] Communicated by the Author.

[†] The Physical Review, June 1913.

"To obtain the conditions of balance, make P=R, then the impedance of the arm b–d must be equal to that of c–d. Let Z equal the impedance of the part of the arm b–d made up of inductance and capacity. We then have

$$\frac{1}{Z}=\frac{1}{Q-iX}+\frac{1}{r+iK}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $X=\omega L$, $K=\frac{1}{\omega C}$, $\omega=2\pi n$, n being the frequency of alternations.

As $P=R$, $Z+s=S$, or

$$\frac{1}{Z}=\frac{1}{S-s}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From (1) and (2),

$$\frac{1}{Q-iK}+\frac{1}{r+iK}=\frac{1}{S-s},$$

or clearing

$$(S-s)(r+iK)+(S-s)(Q-iX)=(Q-iK)(r+iX). \quad . \quad . \quad (3)$$

Equating the reals

$$(S-s)r+(S-s)Q=Qr+XK, \quad . \quad . \quad . \quad (4)$$

whence

$$XK=(S-s)Q+(S-s)r-Qr. \quad . \quad . \quad . \quad (5)$$

From the imaginaries,

$$(S-s)K-(S-s)X=QK-rX,$$

or

$$K[(S-s)-Q]=X[(S-s)-r]. \quad . \quad . \quad . \quad (6)$$

Now it is known that for the bridge to balance the steady current condition must hold, that is, the resistance of the arm c–d must equal that of b–d, i. e.,

$$S=s+Q. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From (6) and (7)

$$(S-s)=r. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

From (5) and (8)

$$XK=r^2$$

or

$$L=Cr^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Thus there are three conditions of balance, as follows :

$$S = s + Q, \quad \text{I.}$$

$$S = s + r, \quad \text{II.}$$

$$L = Cr^2. \quad \text{III.}$$

From I. and II. it is seen that Q must equal r. Thus to balance the bridge set $Q = r$, and then with direct current on the bridge, obtain the steady current balance $Q + s = S$. Then with the alternating E.M.F. applied to the bridge, obtain the inductive balance with either an A–C galvanometer or a telephone."

In trying the experiment I used different capacities and different inductances. The results were at first more or less satisfactory, though there was usually some uncertainty regarding the exact value of Q when obtaining the balance with the telephone. Changing Q by a few ohms one way or the other had often no appreciable effect on the telephone. In such cases the two limits of Q which the telephone could detect were noted and the mean taken as the value of Q.

The significant thing observed in the experiment was the effect of the ohmic resistance of the inductance. When the ohmic resistance was low and the inductance high in comparison more or less good values were obtained, but the inconsistencies become more and more evident as the resistance of the inductance was increased. In the theory given above in obtaining equation (7) for steady current the resistance of L was ignored, for which purpose Q must be very great. As the resistance of L is increased Q also therefore must be increased very much, so that the resistance of L might still remain insignificant in comparison with $Q + s$. In my experiment Q was also therefore increased, but it was found that in that case the sensibility of the balance was sacrificed so much that sometimes when Q was about 2000 ohms it could be altered through 50 or 60 ohms and sometimes more without being quite perceptible on the telephone.

The method is therefore more of a qualitative than of a quantitative value, and the defects noted above much discount the advantages enumerated by the author.

More detailed investigations, theoretical and experimental, are in progress which will be communicated later on.

XVIII. *On the Dependence of the* Kα *Doublet with different Chemical Compounds.* *By* B. B. Ray, *D.Sc., Lecturer, Calcutta University* [*].

It has been found by Lindh [†] that the absorption edges of elements of lower atomic numbers (P, S, and Cl) are not to the same degree as the lines of the X-ray spectra independent of the physical and chemical conditions under which the element in question exists, but that these edges rather depend on such factors as the valency, that is, whether the element in question is monovalent or divalent, etc., in the chemical compound used as anticathode. Recently Lindh [‡], Tandberg [§], and Coster [||] have extended this work to the K and the L absorption edges of other elements. In this connexion Prof. Bohr [¶] writes: "In agreement with what has been brought to light by investigations on absorption of X-rays in elements of lower atomic number, such as have been performed in recent years in the Physical Laboratory of Lund, we understand immediately that the position and eventual structure of the absorption edges will to a certain degree depend upon the physical and chemical conditions under which the element investigated exists, while such a dependence does not appear in the characteristic emission lines." In the measurement of the Kα doublet difference of elements of lower atomic number by Prof. Siegbahn and the author [**], it is found that this difference does not vary from element to element in a quite regular manner in the lower elements, but that there are some sudden changes in the iron group and also in the chlorine group, as may be anticipated from the Bohr model. In this experiment pure metals were used as anticathode so far as they were available, and in the absence of pure metals monovalent salts were used. In this connexion Prof. Siegbahn suggested that there may be a difference in $\Delta\lambda$ of the Kα doublet when different salts, having different valencies for the element in question, are used as anticathodes. The following experiments were undertaken according to his suggestion to find out whether there is any difference in $\Delta\lambda$ for four elements (Cl, K, V, and Fe) under different chemical conditions.

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[*] Communicated by Prof. Manne Siegbahn.

[†] *Diss. Lund,* 1923, also Siegbahn's book, pp. 137-143.

[‡] *Ark. f. Mat. Astr. o. Fys.* Bd. xviii. no. 14.

[§] *Loc. cit.*

[||] *Zeit. f. Phys.* July 1914.

[¶] 'The Theory of Spectra and Atomic Constitution' (Camb. U. Press), p. 120.

[**] *Ark. f. Mat. Astr. o. Fys.* xviii. no. 19.

Experiment.

A Hadding tube was connected to a vacuum spectrograph, the width of the slit being 0·09 mm., and the photographic plate was placed at a distance of 12·15 cm. from the axis of the reflecting face of the calcite crystal. A current of 10 m.a. at about 50 k.v. was passed through the tube from an air-cooled transformer. In order to get sharp images of the Kα_1 and the Kα_2 lines, the time for exposure was necessarily shortened, and in these experiments it only took 10 minutes for all the plates to secure uniform blackness. To put the powdered salt on the copper anticathode, the latter was scratched with a knife and the salt was pressed into the scatches. The anticathode was thoroughly cleaned with a fine iron file when salts were changed, and it was scratched again. This process was repeated whenever new salts were to be put on the copper anticathode. In this experiment only four elements, Cl (17), K (19), V (23), and Fe (26), each having different chemical compositions, were examined.

The following table gives the values of $\Delta\lambda$ for the Kα doublet in X-units :—

Chlorine.

Compound.	$\Delta\lambda$ in X.U.
KCl	3·15
$BaCl_2$	3·15
$KClO_3$	2·99
$Ba(ClO_3)_2$	2·98
$KClO_4$	2·92

Vanadium.

Va Powder	3·68
Am. vanadate	3·60

Potassium.

Compound.	$\Delta\lambda$ in X.U.
KCl	3·40
$KClO_3$	3·22
$KClO_4$	3·16

Iron.

Compound.	$\Delta\lambda$ in X.U.
Fe (powder)	4·20
$(NH_4)_2 Fe(SO_4)_2$.	4·13
$NH_4 Fe(SO_4)_2$ ...	4·01
$K_4 Fe(Cy)_6$	4·06
$K_3 Fe(Cy)_6$	3·99

In this connexion, it may be pointed out that we do not know whether the salts used as anticathode retain their original nature under heavy electronic bombardment. In the above table Cl (17) is monovalent in KCl and $BaCl_2$ and has five valencies in $KClO_3$ and $Ba(ClO_3)_2 + 2H_2O$, and has seven valencies in $KClO_4$ (see Siegbahn's book, p. 142).

So also K (19) is monovalent in KCl and has five valencies in $KClO_3$ and seven valencies in $KClO_4$. The distance between the two Kα lines is measured by a comparator from the photographic plate: only the mean value is tabulated above, the error being less than 1 per cent. It is to be noticed that the value of Δλ decreases as the element investigated attains higher valencies in different chemical compounds.

Changes of α_1 *and* α_2.

The photographic plate holder was then mounted with a fine cross-wire, and in taking the exposure with chlorine and potassium salts it was kept fixed in the required position. In different exposures with different chemical salts, the position of the plate holder was not changed, so that the image of the cross-wire on the photographic plate was formed always at the same angle with KCl, $BaCl_2$, $KClO_3$, $Ba(ClO_3)_2+2H_2O$, $KClO_4$ for chlorine, and with KCl, $KClO_3$, and $KClO_4$ for potassium. The time of exposure in all these plates was only 15 minutes.

The distance between the position of the cross-wire and the corresponding positions of the two lines ($K\alpha_1$ and $K\alpha_2$) was measured by a comparator, and found different for compounds having different valency for the element in question. This shows that the characteristic emission lines are not quite independent of the chemical conditions under which the element investigated exists. It is very difficult to get the exact value of the changes of the $K\alpha_1$ and the $K\alpha_2$ lines, but one can be sure of such changes. In order to find out an accurate value for such a change, a larger number of plates should be examined with many more compounds as anticathodes and possibly with different crystals. The author wishes to examine this point more fully in a future paper.

It gives me great pleasure to thank Prof. Siegbahn for his many valuable suggestions and his keen interest during the progress of the paper. My thanks are also due to Mr. R. Thoraeus for occasional friendly help.

Upsala, Physical Laboratory,
Sweden.

XIX. *On a Dynamical Illustration of the Pressure of Radiation.* *By* E. L. Nicolai [*].

In a recent paper Prof. T. H. Havelock [†] has drawn attention to a dynamical illustration of the pressure of radiation, originally devised by Lord Rayleigh [‡] and Sir Joseph Larmor [§]. One end of a uniform string is fixed, and the string is supposed to pass through a hole in a moving plate. The pressure of radiation on a moving perfect reflector is illustrated by the pressure of the vibrating string on the moving plate. Prof. Havelock finds the value of this pressure by calculating the rate of decrease of energy of the vibrating string; he also points out that the pressure so calculated is less than the resolved force on the plate due to the tension of the string.

What is the reason of the pressure on the plate not being equal to the resolved statical tension of the string? The energy-method gives no answer to this question; in fact the mechanism of the pressure of the vibrating string on the plate remains concealed. In the present note another mode of treatment of the same problem is proposed, which seems to give a clearer idea of the action of the string on the plate. The pressure of the string on the plate can be calculated by the equation of momentum applied to an element of the string which slips through the hole in the moving plate during an infinitesimal interval of time [‖]. It is found that in this mode of treatment second-order terms must be retained; fortunately the transverse displacements of the string are to be calculated to terms of the first order only, so that the usual differential equation of the transverse vibrations of the string remains valid. This method leads to a result in which the well-known formula of Prof. Larmor for the pressure of vibrations on an ideal reflector is included. The result may be slightly generalized by assuming that the plate, while travelling along the string, performs small oscillations in a direction normal to the string. Thus an illustration of the reaction of radiation on a moving source of light is realized.

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[*] Communicated by the Author.

[†] T. H. Havelock, "Some Dynamical Illustrations of the Pressure of Radiation and of Adiabatic Invariance," Phil. Mag. xlvii. p. 754 (1924).

[‡] Rayleigh, "On the Pressure of Vibrations," Phil. Mag. iii. p. 338 (1902).

[§] Sir Joseph Larmor, "On the Dynamics of Radiation," Proceedings of the V. Internat. Congress of Mathematicians (Cambridge, 1913), vol. i. p. 197 (with an Appendix by Prof. T. Levi-Cività).

[‖] A calculation of the pressure of vibrations on this line of argument was given by the author in a note, "On the Pressure of Vibrations," Annals of the Petersb. Polytechn. Institute, xviii. p. 49 (1912) [Russian].

In the paper quoted Prof. Havelock has given a particular solution of the problem of the vibrating string for the case of a fixed and a moving node, the velocity of the moving node being constant. This particular solution corresponds to a normal vibration of the string in the limiting case of infinitesimal velocity of the moving node. It may be shown that the general solution of the problem is made up by a series of particular solutions of the type indicated *.

§ 1. A uniform endless string is stretched along the axis of x; T_0 is its statical tension. The string is supposed to pass through a small hole in a movable plate. The string is performing small transverse vibrations, and the plate travels along the string with (uniform or non-uniform) velocity v. while performing small oscillations perpendicular to the string. The resolved pressure of the string on the plate in the direction of the x-axis is to be calculated.

Let y be the transverse displacement of a point of the string; it is a small quantity of the first order. We shall have to consider longitudinal displacements of the string too; let u be the longitudinal displacement; the string performing transverse vibrations, u is a small quantity of the second order. Let ξ and η be the coordinates of the hole in the plate; they are given functions of the time:

$$\xi = f(t), \quad \eta = \phi(t),$$

η being a small quantity of the first order.

The extension σ of the vibrating string at every point of it is determined to terms of second order by the formula

$$\sigma = \frac{\partial u}{\partial x} + \frac{1}{2}\left(\frac{\partial y}{\partial x}\right)^2.$$

The dynamical tension T of the string is

$$T = T_0 + E\omega\sigma.$$

(E Young's modulus, ω section-area of the string). We suppose the statical tension T_0 to be great, so that $\frac{E\omega\sigma}{T_0}$ is a small quantity (of the first order).

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* This general solution was given by the author in a paper, "On Transverse Vibrations of a portion of a String of uniformly variable Length," Annals of the Petersb. Polytechn. Institute, xxviii. p. 273 (1921) [Russian].

The values of $\frac{\partial y}{\partial x}$ immediately to the left and immediately to the right of the plate will be denoted by $\left(\frac{\partial y}{\partial x}\right)_1$ and $\left(\frac{\partial y}{\partial x}\right)_2$: and similar notations for other quantities (as y, u, $\frac{\partial u}{\partial t}$, σ etc.) will be used.

§ 2. Now let us apply the equation of momentum to an element of the string of length $v\,dt$, which slips through the hole in the moving plate during an infinitesimal interval of time dt. Resolving along the axis of x, denoting the line-density of the string by ρ, and assuming v to be positive when directed from left to right (in the positive x-direction), we find

$$\rho v\,dt\left[\left(\frac{\partial u}{\partial t}\right)_1-\left(\frac{\partial u}{\partial t}\right)_2\right]=[\mathrm{T}\cos\alpha_2-\mathrm{T}\cos\alpha_1+\mathrm{N}_x]\,dt,$$

where α_1 and α_2 are the inclinations of the string to the axis of x immediately to the left and to the right of the plate and N_x is the resolved reaction of the plate on the string.

To terms of the second order we have

$$\cos\alpha_1=\frac{1+\left(\frac{\partial u}{\partial x}\right)_1}{1+\sigma_1}=1-\frac{1}{2}\left(\frac{\partial y}{\partial x}\right)_1^2,$$

and in the same manner we find

$$\cos\alpha_2=1-\frac{1}{2}\left(\frac{\partial y}{\partial x}\right)_2^2.$$

Now putting $\mathrm{N}_x=-\mathrm{P}_x$, where P_x is the resolved pressure of the string on the plate, we have

$$\mathrm{P}_x=\tfrac{1}{2}\,\mathrm{T}\left\{\left(\frac{\partial y}{\partial x}\right)_1^2-\left(\frac{\partial y}{\partial x}\right)_2^2\right\}-\rho v\left\{\left(\frac{\partial u}{\partial t}\right)_1-\left(\frac{\partial u}{\partial t}\right)_2\right\}.$$

This result shows that P_x is a small quantity of the second order. In calculating P_x to terms of the second order only, we may put $\mathrm{T}=\mathrm{T}_0$ and so obtain

$$\mathrm{P}_x=\tfrac{1}{2}\,\mathrm{T}_0\left\{\left(\frac{\partial y}{\partial x}\right)_1^2-\left(\frac{\partial y}{\partial x}\right)_2^2\right\}-\rho v\left\{\left(\frac{\partial u}{\partial t}\right)_1-\left(\frac{\partial u}{\partial t}\right)_2\right\}. \qquad (1)$$

It is to be noticed, that while calculating P_x to terms of the second order we have to calculate y to terms of the first order only. The usual differential equation of transverse vibrations of the string being valid, we have

$$\frac{\partial^2 y}{\partial t^2}=c^2\frac{\partial^2 y}{\partial x^2},$$

with $c=\sqrt{\frac{T_0}{\rho}}$.

Now the condition at the plate $(x=\xi)$ is $u_1=u_2$. Differentiating with regard to time, we find

$$\left(\frac{\partial u}{\partial t}\right)_1+\left(\frac{\partial u}{\partial x}\right)_1\cdot\frac{d\xi}{dt}=\left(\frac{\partial u}{\partial t}\right)_2+\left(\frac{\partial u}{\partial x}\right)_2\cdot\frac{d\xi}{dt}.$$

Now we have

$$\left(\frac{\partial u}{\partial x}\right)_1=\sigma_1-\frac{1}{2}\left(\frac{\partial y}{\partial x}\right)_1^2,\quad \left(\frac{\partial u}{\partial x}\right)_2=\sigma_2-\frac{1}{2}\left(\frac{\partial y}{\partial x}\right)_2^2.$$

Assuming the hole in the plate to be perfectly smooth and accordingly $\sigma_1=\sigma_2$ and putting $\frac{d\xi}{dt}=v$, we obtain

$$\left(\frac{\partial u}{\partial t}\right)_1-\left(\frac{\partial u}{\partial t}\right)_2=\tfrac{1}{2}v\left\{\left(\frac{\partial y}{\partial x}\right)_1^2-\left(\frac{\partial y}{\partial x}\right)_2^2\right\}.$$

By (1) we find

$$P_x=\tfrac{1}{2}\rho(c^2-v^2)\left\{\left(\frac{\partial y}{\partial x}\right)_1^2-\left(\frac{\partial y}{\partial x}\right)_2^2\right\}. \quad . \quad . \quad (2)$$

This result includes the formula of Sir J. Larmor for the case of the ideal reflector; it can also be applied to the case of a travelling source of vibrations. It may be noticed that formula (2) holds good for the case $v^2<c^2$ only, the fundamental assumptions as to the smallness of y, u, $\frac{\partial y}{\partial x}$, etc. being valid only for this case.

§ 3. In Prof. Larmor's case we have $\eta=0$ and $\left(\frac{\partial y}{\partial x}\right)_2=0$, the string being at rest to the right of the plate. We obtain

$$P_x=\tfrac{1}{2}\rho(c^2-v^2)\left(\frac{\partial y}{\partial x}\right)_1^2. \quad . \quad . \quad . \quad . \quad (3)$$

From this result Prof. Larmor's formula is found at once, as is shown in Prof. Havelock's paper. The pressure

P_r, given by (3), is less than the resolved statical tension of the string, which is

$$\tfrac{1}{2}T_0\left(\frac{\partial y}{\partial x}\right)_1^2=\tfrac{1}{2}\rho c^2\left(\frac{\partial y}{\partial x}\right)_1^2.$$

We see now the reason for this fact. Every element of the string, while slipping through the hole in the plate, is gaining momentum in the direction of x. This gain of momentum is due to one part of the resolved statical tension of the string: the other part of the tension produces pressure on the plate.

§ 4. To have a dynamical illustration of a travelling source of light, assume

$$y=F(ct+x)\qquad(-\infty<x<\xi)$$
$$y=\Phi(ct-x)\qquad(\xi<x<\infty).$$

The condition at the plate is $y=\eta$ for $x=\xi$. Hence

$$F(ct+\xi)=\phi(t),\quad \Phi(ct-\xi)=\phi(t),\qquad . \ . \quad (4)$$

and thus the waves F and Φ, emitted by the vibrating plate, are determined.

Now we have

$$\left(\frac{\partial y}{\partial x}\right)_1=F'(ct+\xi),\quad \left(\frac{\partial y}{\partial x}\right)_2=-\Phi'(ct-\xi),$$

and from (4) we obtain

$$(c+v)F'(ct+\xi)=\phi'(t),\quad (c-v)\Phi'(ct-\xi)=\phi'(t).$$

Hence

$$\left(\frac{\partial y}{\partial x}\right)_1=\frac{1}{c+v}\frac{d\eta}{dt},\quad \left(\frac{\partial y}{\partial x}\right)_2=-\frac{1}{c-v}\frac{d\eta}{dt}.$$

Substituting in (2), we obtain

$$P_r=\tfrac{1}{2}\rho(c^2-v^2)\left\{\frac{1}{(c+v)^2}-\frac{1}{(c-v)^2}\right\}\left(\frac{d\eta}{dt}\right)^2=-\frac{2\rho cv}{c^2-v^2}\left(\frac{d\eta}{dt}\right)^2.$$

Let e be the energy radiated by the plate in unit time. We have

$$e=\rho c^2\left(\frac{\partial y}{\partial x}\right)_1^2(c+v)+\rho c^2\left(\frac{\partial y}{\partial x}\right)_2^2(c-v)=\frac{2\rho c^3}{c^2-v^2}\left(\frac{d\eta}{dt}\right)^2.$$

Hence

$$P_r=-\frac{v}{c^2}e,$$

and this is the formula of H. A. Lorentz * and M. Abraham † for the reaction of radiation on a travelling source of light.

§ 5. It may be noticed that the same line of argument, by which formula (2) for the resolved pressure P_x of the vibrating string on the plate in the direction of the x-axis was found, can also be used for a calculation of the resolved pressure P_y on the plate in the direction perpendicular to the axis of x. Using the equation of momentum, we find

$$P_y = -\rho(c^2 - v^2)\left\{\left(\frac{\partial y}{\partial x}\right)_1 - \left(\frac{\partial y}{\partial x}\right)_2\right\}.$$

Applying to the case examined in § 4, we obtain

$$P_y = -2\rho c\frac{d\eta}{dt}.$$

This result accounts for the damping effect of radiation on a source of vibrations.

§ 6. In Prof. Havelock's paper the motion of a string of finite length, one end being fixed and the other passing through a uniformly moving plate, is discussed, and a particular solution of the problem is given. We will show that the general solution of the problem may readily be obtained as a series of terms of the form indicated by Prof. Havelock.

Let $x=0$ be the fixed node and $x=vt$ the moving node (v=const.). We have the differential equation

$$\frac{\partial^2 y}{\partial t^2} = c^2\frac{\partial^2 y}{\partial x^2}$$

with the boundary conditions: $y=0$ for $x=0$ and $y=0$ for $x=vt$.

The general solution is

$$y = F(ct + x) - F(ct - x), \quad . \quad . \quad . \quad . \quad (5)$$

where F satisfies the functional equation

$$F\left(\frac{c+v}{c-v}z\right) = F(z).$$

Now put $z=e^w$, $w=\log z$. Denoting $F(e^w)=\psi(w)$, we have

$$\psi\left(w + \log\frac{c+v}{c-v}\right) = \psi(w).$$

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* H. A. Lorentz, *Enzykl. der mathem. Wissensch.* Bd. v. art. 14, p. 270.

† M. Abraham, 'Theorie der Elektrizität,' Bd. ii. p. 119.

Thus $\psi(w)$ is a periodic function, the period being $\log\frac{c+v}{c-v}$. Expanding in a Fourier series and denoting

$$\frac{2\pi}{\log\frac{c+v}{c-v}}=\alpha,$$

we obtain

$$\psi(w)=\sum_{n=0}^{n=\infty}\{C_n\sin n\alpha w+D_n\cos n\alpha w\},$$

C_n and D_n being arbitrary constants. Hence

$$F(z)=\sum_{n=0}^{n=\infty}\{C_n\sin(n\alpha\log z)+D_n\cos(n\alpha\log z)\}.$$

Substituting in (5), we obtain after some reductions the general solution of our problem in the form

$$y=\sum_{n=1}^{n=\infty}\sin\left[\frac{n\alpha}{2}\log\frac{ct+x}{ct-x}\right]\left\{A_n\cos\left[\frac{n\alpha}{2}\log\left(\frac{t^2}{t_0^2}-\frac{x^2}{c^2t_0^2}\right)\right.\right.$$
$$\left.\left.+B_n\sin\left[\frac{n\alpha}{2}\log\left(\frac{t^2}{t_0^2}-\frac{x^2}{c^2t_0^2}\right)\right]\right\}, \quad . \quad . \quad . \quad (6)$$

t_0 being the initial time (and hence ct_0 the initial length of the string) and A_n and B_n denoting arbitrary constants, related in a simple manner to the constants C_n and D_n.

The constants A_n and B_n are defined by the initial conditions of the problem. Let $y=f(x)$, $\frac{\partial y}{\partial t}=g(x)$ for $t=t_0$ and $0<x<ct_0$. By (5) we easily find

$$F(ct_0+x)=\tfrac{1}{2}f(x)+\frac{1}{2c}\int_0^x g(x)dx, \quad (-vt_0<x<vt_0),$$

where $f(-x)=-f(x)$ and $g(-x)=-g(x)$ is assumed. Also

$$\left.\begin{aligned}A_n&=\frac{2\alpha}{\pi}\int_{-vt_0}^{vt_0}F(ct_0+x)\sin\left\{n\alpha\log\left(1+\frac{x}{ct_0}\right)\right\}\frac{dx}{ct_0+x}\\ B_n&=-\frac{2\alpha}{\pi}\int_{-vt_0}^{vt_0}F(ct_0+x)\cos\left\{n\alpha\log\left(1+\frac{x}{ct_0}\right)\right\}\frac{dx}{ct_0+x}\end{aligned}\right\}. \quad (7)$$

It is easily verified that the limiting values of (6) and (7) for infinitesimal velocity v are the well-known expressions relating to the vibrations of a string of constant length.

Polytechnic Institute, Leningrad,
Sept. 29, 1924.

XX. *On the Permanent Electret.* *By* MOTOTARÔ EGUCHI, *Professor of Physics, Higher Naval College, Tokyo, Japan*[*].

Introduction.

"ELECTRET" is the name given to the dielectric which is electrized[†] permanently by a special treatment due to the author. Some waxes and resinous materials have moderate conductivity in their liquid state, while they are very good insulators in the solid state. The electrical conductivity of these materials varies gradually with the degree of solidification, and when the materials get moderately hard the conductivity becomes practically nil. The author let solidify a mixture of these materials in a strong electric field applied through all the time in which the solidification went on. The dielectric taken out of the field, after having been cooled sufficiently, showed very strong polarities on its two surfaces which were kept in contact with the electrode plates during the preparation. The electrization of such a dielectric could not be destroyed by several treatments, such as touching by Bunsen flame, exposure to X-rays, planing with knife, washing with some solvents, &c. Nor did it die away after the lapse of many years. From several subsequent studies, it has become evident that the electrical change of the dielectric is not of a superficial nature, but that it is a permanent internal change within the material.

The name "Permanent Electret" or simply "Electret" was given to the special dielectric at the ordinary meeting of the Physico-Mathematical Society of Japan, February 21, 1920[‡]. Later, I found in Oliver Heaviside's 'Electrical Papers' the section with the title "Electrization and Electrification. Natural Electret"[§]. In this paper he proposed for the first time to use the term "Electret" to fill the want for describing an intrinsically electrized body, and some possibilities of electrets were discussed on the theoretical points of view. The present method of preparation was, however, obtained independently and also in a way utterly different from his discussions.

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[*] Communicated by the Author.

[†] The term "Electrization" is used after Heaviside to signify the internal electrical change of a material, which is different from superficial electrification.

[‡] Mototarô Eguchi, Phys.-Math. Soc. Japan, ser. 3, vol. ii. no. 7 (1920).

[§] Oliver Heaviside, 'Electrical Papers,' vol. i. § xii.

The electret shows so great an intensity of electrization that the electric force exerted in front of the surface of the electret may attain the greatest sustainable value in the atmosphere. The permanency is also so good that we have detected no sensible decaying for these three or more years since the preparation.

§ 1. *Preparation of the Permanently Electrized Dielectric.*

From the study of the variation of conductivity with the solidification of waxes and some other materials *, I came to think it possible to get a permanently electrified or more correctly electrized dielectric by allowing some kind of waxes to solidify in a strong electric field.

After many trials, it has been ascertained that the disk-shaped electret of a certain size is one of the most convenient forms for several reasons, except for the cases in which special studies are wanted. The method of preparation of the disk-electret is, therefore, briefly described here.

A shallow circular metal basin B (fig. 1), depth 1 cm., diameter 20 cm., is put on a pole-plate P_1, a little larger in diameter than the basin. The plate itself is placed on three sulphur insulators S_1, S_2, S_3, which are laid on a wooden tripod stand T capable of levelling by the three screws f_1, f_2, f_3.

As the other electrode, a hollow metal disk P_2 is suspended by three insulating cords, t_1, t_2, t_3. These cords are made of Japanese fishing-lines, Tegusu (a kind of thick silk thread), whose surfaces have been treated with a mixture of some waxes and resin to get rid of the surface leakage. The basin and the disk-electrode are coated with tin-foils (not shown in the figure). The lead sheet L is used as a weight to cause the foil tightly to attach itself to the disk.

As the preparatory adjustment, the levelling of the basin B is first effected by three screws f_1, f_2, f_3; secondly, the hook at the end of the cord C is transferred from the arrester h_1 to another h_2, and the plate P_2 is so regulated by three screws Sc′, Sc″, Sc‴ that its lower surface comes just up to the margin of B. Another cord C′ stretched through a hole perforated near the end of the guider *g* serves to prevent the oscillation of the electrode P_2.

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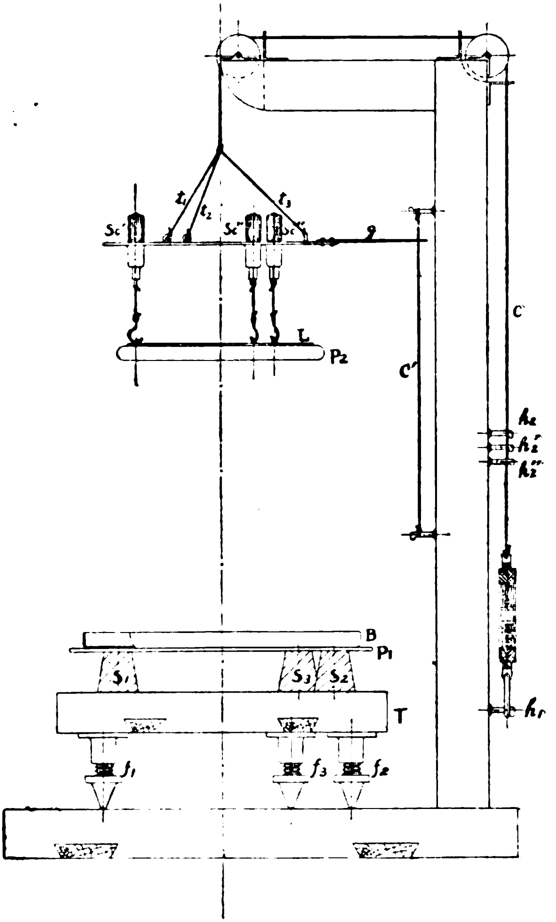
* Mototarô Eguchi, Phys.-Math. Soc. Japan, ser. 3, vol. i. nos. 10-11 (1919).

Fig. 1.



After raising the disk-electrode P_2 up to a sufficient height, the material melted at a temperature far above its melting-point (about 130° C.) is poured in to fill up the basin B, and then P_2 is put on the melted dielectric so that it rests just on the surface of the dielectric. The air bubbles, if any, on the surface of the melted material may be easily taken off by touching with a small Bunsen flame.

Care was taken to adjust the voltage of the high tension source in order to prevent any undesirable effect such as brush discharges between the electrodes along the surface of the dielectric when it solidified partially. Tin-foils were applied on the electrodes, so that not only did the dielectric not adhere directly to the metal surface, but it might also contract freely as it cooled, and when the dielectric solidified completely the disk-shaped material might be easily taken off from the basin. Moreover, with the disk-electret thus obtained, both surfaces upper (U) and lower (L) might be studied at will.

§ 2. *The Charge of Temporary Nature and the Permanent Electrization of the Electret.*

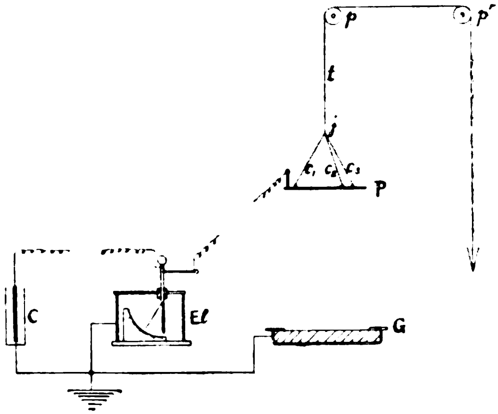
As the material for the permanent electret, a mixture consisting of equal parts of carnaüba-wax and resin with or without a certain amount of bees'-wax was found to be very good as regards the intensity of electrization and the permanency. If we prepare a disk-electret of this material, joining for instance the upper surface (U) to the positive pole of the high tension source, and the lower surface (L) to the negative, we first detect in general a surface charge of negative sign on the upper surface, and one of positive sign on the lower, soon after we take the electret out of the preparing arrangement. But these kinds of charges are of temporary nature, and they die away gradually, in a comparatively short time (in one or two days). After the complete decay of such charges, the surface charges of opposite signs respectively to the above gradually grow up. The positive charge on the upper surface and the negative on the lower, which are respectively of the same signs as those of the applied poles of the source during the preparation, tend to grow to their ultimate values in a few days. The manner of growth of these charges on both surfaces and their values do not vary much even when the method of preparation is modified in some way: for example, when both electrodes are completely insulated from the earth, or when either one of the electrodes is completely earthed and the other insulated. The permanency of these charges is so good that we cannot detect any sensible decay after many years, as will be shown later on (see § 8). We shall call these surface charges of the electret the free charges due to its proper electrization.

§ 3. *On the Method of Measuring the Surface Density of the Free Charge.*

Before entering upon the details of the behaviour of the electret, it will be convenient to describe the method of measuring the surface density of the free charge which was found to be the most simple and reliable.

The arrangement is shown in fig. 2. P is an induction plate of a circular form, diameter 12 cm., with a guard-ring G. The induction plate may be kept at any desired height by means of three insulating suspension cords c_1, c_2, c_3, and a thread *t* attached to the common joint *j* of these cords, passing over pulleys *p* and *p′*. The size of the plate was chosen so large that the electrization of the portion of the dielectric under the plate was quite uniform, and the guard-ring G with a small air-gap was employed for eliminating the end effect on the induction plate. To the induction plate, a calibrated electrometer El and a variable condenser C are connected by means of soft springs of thin wires. Putting the disk-electret together with its metal basin in the proper position under the induction plate, the earthed guard-ring is first laid on the surface to be measured. The induction plate is then put in its position on the surface, the system being always kept earthed during this process. Disconnecting the earth line of the plate system, and lifting the plate to such a height that the influence of the dielectric on the plate was no longer sensible, the electrometer reading

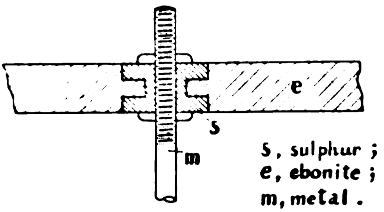
Fig. 2.



was taken. As to the insulation of the condenser, special care was taken to get rid of the surface leakage. The metal rods of the condenser plates were suspended through the central holes of the sulphur pieces moulded in the form shown in fig. 3.

Such a moulded piece of sulphur has a sufficient mechanical strength, and it was ascertained that the condenser might be used in any wet atmosphere without fear of any appreciable leakage.

Fig. 3.



The surface density σ of the free charge of the electret may be calculated from the observed numbers as follows :—

$$\sigma=\frac{C.V}{\pi r^2},$$

where C is the capacity of the condenser system, V the potential read by the electrometer, r the effective radius of the circular surface of the induction plate (radius of the plate + one-half of the air-gap). Any conducting agent, such as moisture, dust, free ions, &c., if present on the dielectric surface, may reduce the electrostatic induction on the plate. It is very difficult to keep the surface quite free from such disturbances. Moreover, the irregularity of the surface of the electret may have an influence on the induction of the plate. The value of σ estimated as above may, therefore, be somewhat smaller than the true value.

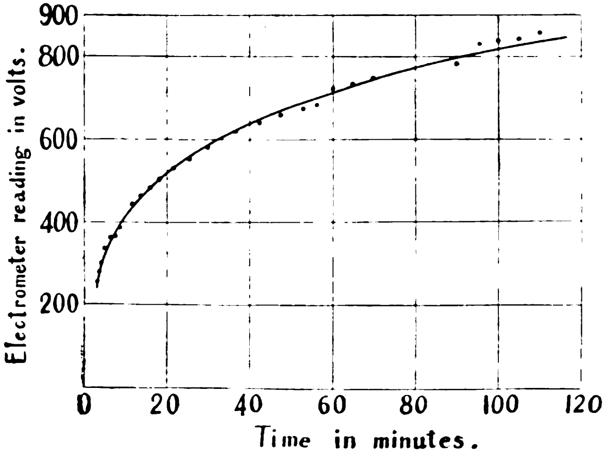
The sign of the induced charge was determined every time and that opposite to this sign was taken as that of the free charge.

· § 4. *Action of X-rays on the Electret.*

If the surfaces of a disk-shaped electret are exposed to X-rays for some time, the free charges on the surfaces apparently disappear. The surface density of the free charge reappears, however, gradually, and attains its final proper value estimated before the exposure. However many times the exposures are repeated, the recoveries are always complete. By the time of exposure, the nature of the X-rays and the intensity of the rays, the rate of recovery is influenced in greater or less degree. But in any case, when the free charge has recovered itself completely, the final surface density is always the same, and shows a definite value proper to the electret.

Several methods of exposing the disk-electret to X-rays were tried. In one case, the X-rays were sent in the direction normal to the disk-surface, allowing the rays to pass through the dielectric material. In another case, the X-rays were let go along the disk-surface, the edge of the disk being protected from the rays by a lead band of a sufficient breadth, and thus the rays were cut off and could not go through the dielectric material. In either case, we did not find any material difference in the temporary disappearance of the free charges and their spontaneous recoveries.

Fig. 4.



This temporary disappearance of the free charge and its recovery afterwards might be explained on the view that the ions in air produced by X-rays are caught on to the surface by the charges of opposite sign respectively, and when the action of the X-rays ceases, the ions fly off spontaneously from the surface by their kinetic energy of agitation, opposing the electrostatic attraction of the free charges of the dielectric surfaces on the ions. A few examples of the observed facts are given below.

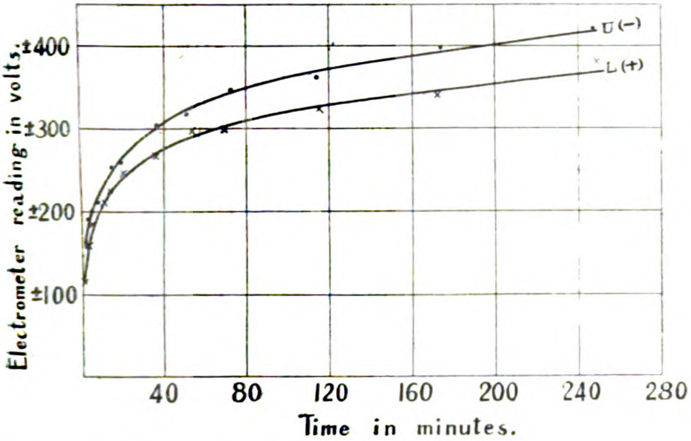
In fig. 4 the time curve of the recovery of the free charge after an exposure to very soft X-rays is plotted, the surface of the disk-electret being kept bare during the recovery. The recovery obeyed very nearly an exponential law,

$$V' - V = (V' - V_0)e^{-\lambda t},$$

where V is the potential of the electrometer at time *t*, and V′ the final potential which corresponds to the ultimate free charge.

In fig. 5 the simultaneous recoveries of the charges of both surfaces, upper and lower, of one disk-electret are given.

Fig. 5.



The small difference of the ultimate values of the surface densities for the two surfaces will probably be due to the difference of the condition of the two surfaces, such as the non-uniformity of the electrization near the rim of the surface, &c.

§ 5. *Evidences for Permanent Internal Electrization in the Dielectric.*

Many experimental studies were carried out for testing the author's view that the electrification measurable as the surface density of opposite signs appearing respectively on the two surfaces of the special electret are the free charges of the permanent electrization within the material. The brief description of the results of these studies will be given below.

(1) Temporary disappearance of the free charges by X-ray exposure and their complete recovery after the withdrawal of the rays (as stated in the preceding section).

(2) The behaviour of the free charges after the treatment of the surface by a Bunsen flame is very similar to the effect of X-ray exposure.

When the surface of the electrized dielectric was treated with a Bunsen flame in such a degree that some surface layer of the dielectric material was melted and again solidified after the withdrawal of the flame, the surface charge was very much reduced, or sometimes it completely vanished, if measured soon after the treatment. This disappearance was, however, only temporary, and the free charge recovered itself, as was seen in the case after an X-ray exposure.

(3) Effect of planing with knife.

I planed with a sharp knife both upper and lower surfaces of an electrized dielectric to some depth, so that the old surfaces no longer remained. The free charges were apparently reduced to a small amount, but they recovered gradually as they did after the exposure to X-rays, the only difference from the latter case being that the recovery was somewhat irregular. When the free charges had recovered completely, I tried the knife treatment once more to the depth of some mms., after which the recovery was also similar and perfect, and the ultimate values of the free charges were very near to those before the treatment.

(4) Effect of washing with some reagents.

I studied the effects of washing the electret surfaces with some reagents such as water, acids, alkalis, absolute alcohol, ether, benzene, &c. Though the free charges disappeared after such a treatment, they always recovered some time after the dielectrics were made completely dry. The results were, thus, also affirmative for the permanent internal electrization of the material.

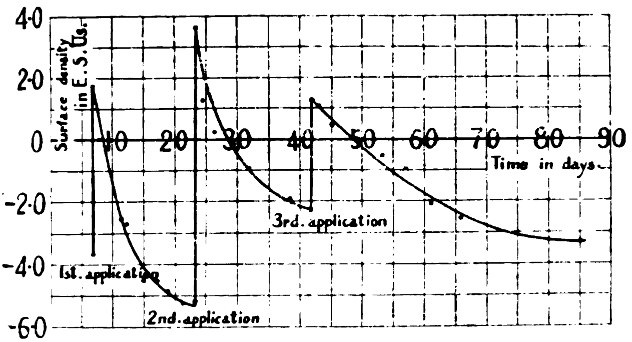
(5) Comparison of two pieces of dielectrics of the same materials, one of which was electrized by the special treatment, the other merely superficially charged by means of an ordinary process.

The dielectric material was solidified in a metal basin under conditions otherwise the same as in the preparation of the special electret in every respect, but applying no electric field. After the solidification was completed, the material was put under the action of an electric field for a sufficiently long time of one hour or more. Such a dielectric, soon after the treatment, takes strong surface charges of opposite polarities on its surfaces. Though these surface charges displayed some weak residual charges, their intensity and durability were of very small order quite incomparable with those of the electret.

(6) Effect of electric force on the electret.

Different electric forces were applied on some disk-electrets, and the effect of such forces on the electrization of the material was observed. I took two of them of which the sense of electrization was known. For convenience' sake, the electric force in the same sense as the field employed in the preparation for an electret will be called "positive," and that of the opposite sense "negative." To the first disk A_3 a negative electric force was applied for thirty minutes, and afterwards the variation of the free charges was observed. The results of the observation repeated three times successively are plotted in fig. 6, the surface density of the upper surface U only being shown in the figure, since the other surface L showed a behaviour similar to U in every respect but with the sign of its charge opposite.

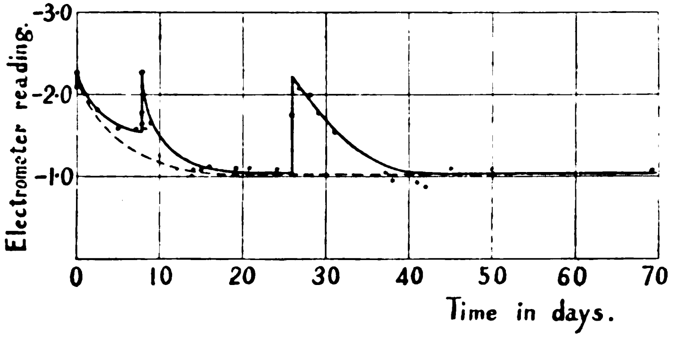
Fig. 6.



As we see on the figure, seven days after the preparation, the disk had a free charge of negative sign on surface U and of positive on L, nearly settled at their full values. By the application of the negative electric force for thirty minutes, the surfaces got moderately large surface densities of the signs respectively opposite to those of the free charges of the proper electrization. These temporary charges, however, decayed rapidly, and the gradual growth of the surface charges due to the original electrization followed. When the rate of growth of the surface charge became very small, the second and the third applications of the negative electric forces were tried successively, and the results were always of the same nature as in the first application.

With the second disk W_2, the effect of applying the positive electric force was studied. Though small temporary increases of the surface charges were observed after the application of this force, they settled rapidly to their proper value due to the electrization. The results are depicted in fig. 7.

Fig. 7.



From these experiments we may safely conclude that, by the application of an electric force, positive or negative, on a prepared electret, the surface electrification may be disturbed in some degree, but the permanent electrization of the electret remains almost unaffected.

§ 6. *On the Intensity of Electrization of the Permanent Electret.*

From many experimental studies made by the author * the internal electrical change of the permanent electret was concluded to be of the nature of "polarization," *i. e.* every portion from element to element of the dielectric material was in a state of having acquired equal and opposite electrical polarities on its two ends.

The surface density of the free charge measured by means of the method described in § 4 may, therefore, be taken as the intensity of permanent electrization within the dielectric. Most electrets of which the materials consist of carnaüba-wax and resin with or without some percentage of bees'-wax, have so great intensities of electrization that they exceed the greatest possible surface densities of the electrifications charged on some good insulators such as sealing-wax, shellac, sulphur, &c., by means of mechanical friction. The following numbers are given to show the comparison of these surface densities.

* Mototarô Eguchi, Phys.-Math. Soc. Japan, ser. 3, vol. v. no. 8 (1923).

TABLE I.

Maximum attainable surface densities by mechanical friction *.

Material.	Rubbed on wool. Max. surf. density.	Rubbed on silk. Max. surf. density.
Sealing-wax	5·70 E.S.U.	5·40 E.S.U.
Shellac	5·57 ,,	5·12 ,,
Sulphur	5·48 ,,	5·39 ,,
Ebonite	4·82 ,,	4·43 ,,
Amber	4·18 ,,	4·11 ,,
Glass	2·65 ,,	2·90 ,,

TABLE II.

Surface densities of the free charges of the internal electrization of the permanent electrets.

Disk-electret O_1, prepared Oct. 27, 1919.

Date (*d*).	Time since the preparation (*t*).	Surf. (*s*).	Surf. density (σ).	Electric intensity in air in front of the surf. (E).
Mar. 22, 1921...	$1^{\text{y.}}\ 5^{\text{mon.}}$	U	−5·7 E.S.U.	−72 E.S.U.
		L	+6·2 ,,	+78 ,,
Mar. 3, 1922...	$2^{\text{y.}}\ 5^{\text{mon.}}$	U	−6·5 ,,	−82 ,,
		L	+6·2 ,,	+78 ,,

Disk-electret R_1, prepared Oct. 30, 1919.

d.	*t*.	*s*.	σ.	E.
Mar. 22, 1921...	$1^{\text{y.}}\ 5^{\text{mon.}}$	U	−5·6 E.S.U.	−70 E.S.U.
		L	+5·6 ,,	+70 ,,
Mar. 3, 1922...	$2^{\text{y.}}\ 5^{\text{mon.}}$	U	−6·0 ,,	−75 ,,
		L	+5·8 ,,	+73 ,,

The electric intensities in air in front of the surfaces of the electret are calculated from $E=4\pi\sigma$, and are given in the last column in the above table. Lord Kelvin found that the electric intensity sustainable in air was 130 E.S.U., and therefore the corresponding surface density was 10 E.S.U. These numbers might, however, hardly be realized in a very good condition of air. The numbers of the permanent electrets are not much smaller than these limiting values. It will be observed, in what a higher order of intensity of electrization the electrets are than the ordinary residual electricities in dielectrics hitherto known.

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* L. Graetz, *Handbuch der Elektrizität und des Magnetismus*, Bd. i. Saite 10 (1918).

§ 7. *On the Permanency.*

The disk-shaped electrets are kept usually with their surfaces covered with earthed tin-foils. Under this surface condition, the surface density of the free charge of the electrization remains nearly constant for many years, though small fluctuations may occur probably due to the atmospheric conditions such as the temperature and humidity. Some disk-electrets were tested by keeping them in this condition during three years or more since their preparation, their surface densities being measured at moderate intervals. No natural decay of the surface densities was observed. In the following table two examples of the records of the electrets kept in such a condition are given.

TABLE III.

Surface density of the free charge of the electrization.

Disk-electret O_1.

Date………	Oct. 27, 1919.	Dec. 23, 1920.	Dec. 24, 1921.	Mar. 3, 1922.	Dec. 20, 1922.
Surf. density in E.S.U. or other remarks.	prepared	U −4·5 L +5·6	U −5·8 L +5·1	U −6·5 L +6·2	U −5·1 L +7·2

Disk-electret R_1.

Date………	Oct. 27, 1919.	Dec. 23, 1920.	Dec. 24, 1921.	Mar. 3, 1922.	Dec. 20, 1922.
Surf. density in E.S.U. or other remarks.	prepared	U −5·1 L +5·6	U −5·8 L +4·7	U −6·0 L +5·8	U −6·2 L +7·2

If the electret is kept with its surfaces bare the surface density apparently decays in some degree. The final reduced value of the surface density seems, however, to be kept at some amount different from zero. It is worth noticing that, for observing these decays definitely, it is necessary to keep the electret on some pointed supports in a dry and dust-free air in a desiccator. Otherwise a coating of dust attracted by the free charge behaves as an earthed conductor.

If an electret, whose free charge has thus decayed to a small amount, is again kept covered with tin-foils applied on both surfaces the free charge recovers itself gradually, and at last its surface density attains its proper value. The length of time during which the surfaces are kept bare may affect somewhat the rate of recovery of the surface density when the electret is again covered. The final surface density seems, however, to take the definite value proper to the electret.

The disk-electret M_2 was taken for this kind of tests, and the results are given in Table IV.

Table IV.

Disk-electret M_2.

Date...	Nov. 30, 1920.	Dec. 10, 1920.	Dec. 15, 1920.	Dec. 18, 1920.	Oct. 18, 1921.
Surf. density in E.S.U. or other remarks.	prepared	U −5·1 L +6·7	U −4·2 L +5·8	U −2·5 L +2·5	U −0·1 L +0·05 both surfaces cleaned with feather brush and then exposed to X-rays.
Surf. condition.	← kept covered with tin-foils. →		← kept bare in ordinary atmosphere; both surfaces were coated with dust. →		

Date	Oct. 22, 1921.	Nov. 12, 1921.	Jan. 14, 1922.	Jan. 30, 1922.	Mar. 6, 1922.
Surf. density	U −0·2 L +0·1	U −3·5 L +3·1	U −0·1 L +0·08	U −2·5 L +1·9	U −4·2 L +3·2 surf. density moderately great; permanency good.
Surf. condition	kept in a desiccator with both surfaces covered. →	← kept in a desiccator with surfaces bare. →	← kept in a desiccator with surfaces covered. →		

Summary.

1. The Permanent Electret was made of a certain mixture of wax and resin, keeping it in a strong electric field during its solidification.

2. The nature of the electrical change of the dielectric is a permanent internal electrization of the material entirely different from the superficial electrification.

3. The electrization cannot be destroyed by different treatments applied on the surface such as Bunsen-flame treatment, X-ray exposure, washing with some solvents, planing with knife, applying electric force in any sense, &c.

4. The intensity of electrization of the electret attains such a high degree that the electric intensity in air in front of the electrized dielectric takes nearly the greatest sustainable value.

5. The permanency of the electrization is also extremely

good, so that we have detected no decaying for three years or more since the preparation.

In conclusion, the author wishes to express his best thanks to Dr. Terada, Prof. of Tokyo Imperial University, and Dr. Honda, Prof. of Tohoku Imperial University, for their continued interest in the present investigation.

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XXI. *Abnormal Reflexion of X-Rays.* By J. H. SMITH, *M.Sc., Assistant Lecturer in Physics, University College, London* *.

CLARKE and DUANE† have found, by the ionization spectrometer method of Bragg, certain diffraction maxima which do not obey the two laws governing the Bragg maxima, namely—the angle of incidence equals the angle of reflexion, and that the orders of spectra are given by

$$n\lambda = 2d \sin\theta,$$

where λ is the wave-length of the rays and d the distance between planes concerned.

Prior to this Duane ‡ had discovered maxima obeying the Bragg laws, but due to characteristic radiation produced by fluorescence of atoms in the crystal.

If this set of maxima exists it is easily shown that an "abnormal" set must also exist; and also that this second set will be of greater intensity than the first set. This abnormal set also exists when there is no fluorescence.

These abnormal maxima are due to the periodicity of scattering centres in the planes themselves, and, unlike the main Bragg maxima, the positions of the abnormal sets will vary as the crystal is rotated about the normals to the planes producing them.

Consider a plane wave of homogeneous radiation incident on a set of planes a distance d_2 apart, at a glancing angle θ. Bragg § considers each plane as continuous, and this is sufficient for the set of maxima which is primarily related to d_2. For the general maximum the planes of spacing d_2 can be considered as made up of scattering centres with a spacing d_1 in the plane of incidence.

* Communicated by the Author.

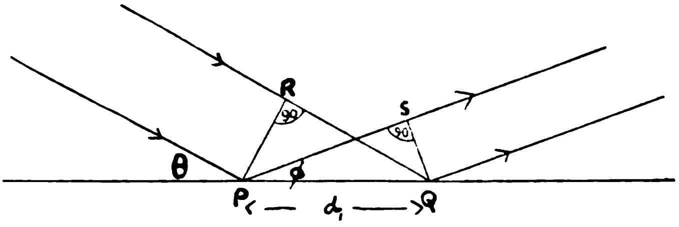
† Proc. Nat. Acad. Sci. ix. 4. p. 131 (1923).

‡ Proc. Nat. Acad. Sci. viii. 5. p. 90 (1922).

§ 'X Rays and Crystal Structure,' 2nd edition, p. 12.

The first condition that there shall be a maximum in any direction making an emergent glancing angle ϕ is then :

Fig. 1.



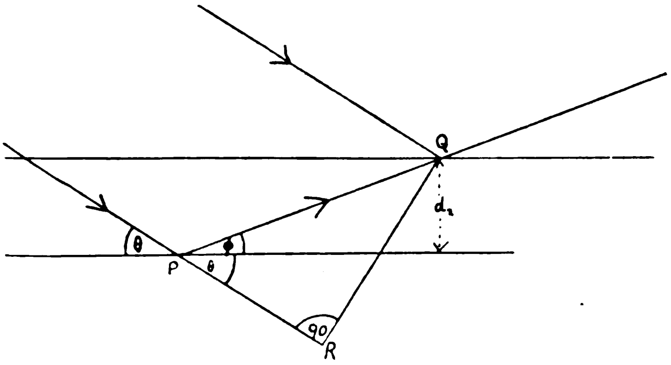
$$PS - RQ = n_1\lambda, \quad \text{where} \quad n_1 = 0, 1, 2, \text{etc.} ;$$

$$i.e., \qquad \cos\phi - \cos\theta = n_1\lambda/d_1 ;$$

$n_1 = 0$ gives the Bragg maxima, and is independent of d_1.

Instead of Bragg's second condition, the relation will be

Fig. 2.



$$PQ - PR = n_2\lambda, \quad \text{where} \quad n_2 = 1, 2, 3, \text{etc., but not } 0;$$

$$i.e., \qquad \frac{1}{\sin\phi} - \frac{\cos(\theta+\phi)}{\sin\phi} = \frac{n_2\lambda}{d_2},$$

which gives the Bragg maxima when $\theta = \phi$.

If d_1 and d_2 are known, the values of θ and ϕ corresponding to various values of n_1 and n_2 can be found.

In order to explain the first set of fluorescent maxima Clarke and Duane assume that there is a definite phase relation between the absorbed wave and the emitted phosphorescent radiation. Their first set of maxima, which obey the Bragg laws, must be due to the interference of this fluorescent radiation with the same radiation scattered from atoms other than its source. The abnormal maxima will be due to the interference of the initial fluorescent radiation without any secondary scattering, and will thus be of greater intensity than the first Duane set.

The laws obeyed will be similar to those above. If λ_1 is the wave-length of the incident radiation and λ_2 that of the fluorescent radiation, the two conditions become

$$\frac{\cos\phi}{\lambda_2}-\frac{\cos\theta}{\lambda_1}=\frac{n_1}{d_1}$$

and

$$\frac{1}{\lambda_2\sin\phi}-\frac{\cos(\theta+\phi)}{\lambda_1\sin\phi}=\frac{n_2}{d_2},$$

with n_1 and n_2 as before.

Since Duane used white radiation it is impossible, from his data, to do more than show that the various values of λ_1 lie within the limits of his spectral range.

McKeehan* has solved the question of abnormal maxima for a cubic lattice only. The above method is applicable to any system.

XXII. *The Mutual Action of Charged Particles in Liquid Media.* *By* Professor E. F. Burton *and* J. E. Currie, *M.A.*†

I. *Electroendosmose and Related Phenomena.*

THE term electroendosmose is applied to the phenomenon of the transfer of liquids through capillary tubes under the action of an electric field set up throughout the tubes by electrodes placed at the ends of the tubes and maintained at a given difference of potential. The experiments on single capillary tubes have been extended to porous diaphragms which are treated merely as collections of fine capillaries. The laws governing this action have been very fully worked out by a succession of scientists.

Although this phenomenon of electroendosmose has been given particular attention, it is merely one of four phenomena which treat of the electrical forces set up by the relative motion of solids and liquids or of such relative motions set up by applied electromotive forces. The correlation of these phenomena may be seen in Table I.

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* Opt. Soc. Amer. and Rev. Sci. Inst. Dec. 1922, p. 989.

† Communicated by the Authors. Read before joint session of Sections A and B, British Association for the Advancement of Science, Toronto meeting.

TABLE I.

A.	B.
Motion caused by applied E.M.F.	E.M.F. set up by impressed motion.
I. Liquid moving through stationary solid tubes. Electroendosmose (1).	I. Liquid forced through stationary solid tubes. Helmholtz-Billiter (3).
II. Solid particles moving through stationary liquids. Cataphoresis (2).	II. Solid particles dropped through stationary columns of liquid. Dorn effect (4).

(1) Wiedemann, *Elektricität*, i. p. 1007 (1893).
Quincke, *Pogg. Ann.* cxiii. p. 513 (1861).
Helmholtz, *Ann. d. Phys.* vii. p. 337 (1879); Memoirs Lon. Phys. Soc. 1888.
Lamb, Brit. Assn. Rep. p. 495 (1887).
Perrin, *Jour. Chim. Phys.* ii. p. 607 (1904); iii. p. 50 (1905).
Elissafoff, *Zs. f. Phys. Chem.* lxxix. p. 385 (1912).
Briggs, Bennett, and Pierson, J. of Phys. Chem. xxii. p. 256 (1918).
(2) Burton, Physical Prop. of Coll. Sol. (Longmans, Green, 1921, p. 132).
M. E. Laing, J. of Phys. Chem. xxviii. p. 673 (1924).
Mukherjee, Proc. Roy. Soc. A, ciii. p. 102 (1923).
(3) Freundlich, *Kapillarchemie*, 3rd ed. p. 335.
Helmholtz, *loc. cit.* (1).
Billiter, *Zs. f. Phys. Chem.* xlviii. p. 542 (1904).
(4) Freundlich, *Kapillarchemie* (loc. cit.).
Dorn, *Ann. d. Phys.* v. p. 20 (1878); ix. p. 513 (1880); x. p. 46 (1880).
Billiter, *Ann. d. Phys.* xi. p. 937 (1903).
Freundlich and Mäkelt, *Zs. f. Elektroch.* xv. p. 161 (1909).

It is at once apparent that there is an intimate relation existing between these phenomena, B being in general the converse of A, and within both A and B, (II.) is the converse of (I.).

The common feature of all these phenomena is illustrated by the explanation which has been offered by the so-called Helmholtz double layer.

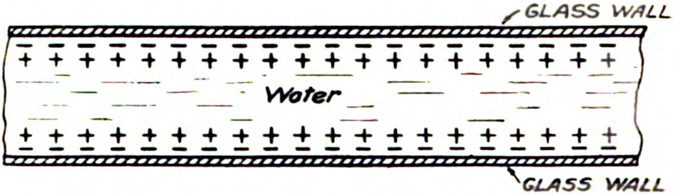
II. *The Helmholtz Double Layer.*

Historically the discussion of electroendosmose and cataphoresis came first (Wiedemann, *l. c.*). In order to explain these curious motions, Quincke (1) suggested that the solid in contact with the liquid became charged in some way with electricity of one sign, while in the immediate vicinity of the solid wall there was a layer of electrical charges of the opposite kind, exactly equal in magnitude to the first. Helmholtz (1) first offered a mathematical treatment of Quincke's suggestion and arrived at certain formulæ the truth of which could be—and, in fact, was—tested and proved to be true. The picture presented is consequently known as the Helmholtz double layer, which was further amplified several years ago by Lamb (1).

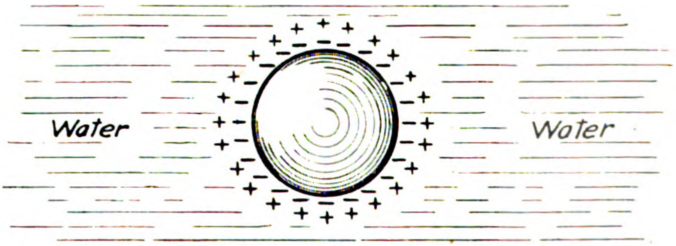
When two electrodes, positive and negative, maintain a difference of potential at the ends of the capillary tube, the liquid is dragged through towards the negative electrode and slips as a sleeve through the tube. A similar but rather more fantastic explanation was offered of the movement of solid particles through stationary liquid media.

Fig. 1.

HELMHOLTZ DOUBLE LAYER



ELECTROENDOSMOSE IN CAPILLARY TUBES



PARTICLES IN WATER

The assumption adopted by both Helmholtz and Lamb, in which they have been followed by others, is that the total thickness of the double layer is just of molecular dimensions, *e.g.*, it is assumed that the charged particle plus its double layer gives an entity which is electrically neutral. This assumption of the thickness of the layer is not implied in the Helmholtz test formula for electroendosmose, which is as follows * :—

$$v = \frac{r^2 \epsilon D E}{4 \eta l},$$

---

* Freundlich, *Kapillarchemie*, 3rd ed. p. 329.

where

v = volume of liquid transported per sec. through a tube of radius r and length l;
η = coefficient of viscosity of the liquid;
D = dielectric constant of liquid;
ϵ = difference of potential between stationary charged layer and the outer Helmholtz layer;
E = the electromotive force applied to electrodes at the ends of the capillary tube.

Consequently, the fact that this formula has been found to hold true for various experimental tests does not demand one's assent to the assumed thickness of the outer layer.

Comparatively recently, the theory of the double layer has been dealt with quite fully by Gouy [*], Chapman [†], and Debye and Hückel [‡].

In discussing the distribution of charges at the surface of contact of a metal electrode and water, Gouy takes for granted that there is a surface charge distributed over the metal electrode, but with regard to the Helmholtz double layer he remarks that "the outer layer of charge cannot be purely superficial, but the ions of this layer are subjected to two sets of forces, those electrical tending to make them accumulate in a layer immediately contiguous to the electrode and those of diffusion, which tend to re-establish the original conditions, *i.e.* uniform distribution of positive and negative ions." For example, if the solid wall is negatively charged, there will be a distribution of negative electricity immediately on the solid wall; this will tend to attract to the immediate neighbourhood a counterbalancing number of positive ions and repel the negative ions. However, diffusion forces intervene so that, if one could proceed from the wall into the liquid, one would pass through a layer rich in positive ions, poor in negative but not entirely devoid of negative, and, as one got further and further from the wall, the distributions of positive and negative ions would tend to become equal. Defining the distance of the centre of gravity of the outer layer as the distance at which an infinitely thin layer of ions equal in total charge to the outer Helmholtz layer must be placed in order that it should exert the same electrical force as the real distribution, Gouy deduced a formula for this distance, which serves as an index of the distribution of this outer layer. A numerical calculation for a very likely distribution of electricity on a solid wall, viz. 10 e.s. units of charge per sq. cm., gives for the distance of the centre of gravity*:

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[*] Gouy, *Jour. de Phys.* (4) ix. p. 457 (1910).
[†] Chapman, Phil. Mag. xxv. p. 475 (1913).
[‡] Debye and Hückel, *Phys. Zeit.*, Feb. 1, 1924.

For $\frac{N}{10}$ solution of salt:—

$$0\cdot96\,\mu\mu = \cdot00096\,\mu = 9\cdot6\times10^{-8}\text{ cm.}$$

,, $\frac{N}{100}$ solution of salt:—

$$9\cdot6\,\mu\mu = \cdot0096\,\mu = 96\times10^{-8}\text{ cm.}$$

,, pure conductivity water:—

$$1010\,\mu\mu = 1\cdot01\,\mu = 1\cdot01\times10^{-4}\text{ cm.}$$

Modern opinion consequently has departed from the position that the thickness of the double layer is of the order of one or two molecular diameters.

III. *The Mutual Action of Suspended Particles.*

In order to explain the phenomenon of cataphoresis, Helmholtz (1), after postulating the double layer, says "On the whole, the algebraic sum of the two (charges on the two layers) equals zero, and the centre of gravity of the complete system, solid particle and surrounding positively charged fluid layer taken together, cannot be moved by the electric forces which arise from the potential fall in the liquid through which the current passes. However, the electric force will tend to bring about a displacement, relatively to each other, of the positively charged fluid layer and the negatively charged particle (or *vice versa*), whereby the fluid layer follows the flow of positive electricity while the positive moves in the opposite direction. If the liquid were a perfect insulator the new position would still be a condition of equilibrium. Since, however, through the displacement of the layers, the equilibrium of the galvanic tension between the solid particle and the liquid is disturbed, and, on account of the conductivity of the liquid, always seeks to restore itself, the original state of electrical distribution will tend to be continually reproduced and so new displacements of the particle with respect to the surrounding liquid will continually occur."

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* *Note.*—The limiting concentration of aqueous colloidal solutions of gold, silver, and platinum is of the order of 20 mgm. per 100 cc. If in a platinum solution the particles are spheres of radius 10^{-6} cm. the least distance between the particles is 100 times their radius and quite the order of distance at which we should expect the mutual repulsion to become active if Gouy's ideas are correct.

One direct result of the above theory is the suggestion reiterated by most colloidal chemists (see Svedberg*, Porter†) that there cannot be any mutual repulsion between colloidal particles, due to the possession of like electrical charges. But, if we accept the ideas suggested by Gouy, we must admit such electrical repulsion whenever the particles approach one another within a distance represented by twice the distance of the centre of gravity of the outer Helmholtz double layer—a distance which might easily become large compared with the diameter of colloidal particles.

In fact, the suggestion of mutual attraction of particles on near approach to one another has been put forward by Smoluchowski ‡ in his paper on the "Mathematical Theory of Coagulation," an assumption to which he was driven by a denial of the existence of mutual repulsion of such particles if they approach one another sufficiently.

Whether one denies mutual repulsion or not it is an undisputed fact that the particles of a stable colloidal solution do remain apart, although they are executing the Brownian movements and, one would judge, are being driven continuously into collision. Smoluchowski made the following assumption: "The simplest assumption would be perhaps that the particles, on near enough approach to one another, are drawn together by capillary action; that union does not take place under normal conditions might be explained by a protective action of the electrical double layer, *which one can picture to one's self as a sort of shell.* On adding electrolytes, on account of the Freundlich absorption, a partial or complete discharge of the double layer takes place, which destroys its protective action, so that collisions and coalescence ensue. .... We shall assume that each particle is surrounded by a protective sphere, so that neighbouring particles execute their proper Brownian movements independently and undisturbed, so long as each one keeps without the protective spheres of its neighbours. But two particles are indissolubly united as soon as one of them pierces the boundaries of the protective region of a neighbouring particle."

A more logical view of the distribution of ions in the Helmholtz double layer gives a far simpler and more acceptable explanation of the facts. Gouy's view of this distribution enables us to look upon single colloidal particles as bearing on their surface an effective charge which cannot be regarded as being neutralized by the outer Helmholtz layer until a surface is reached at such a distance from the boundary of the particle that the distribution of positive and negative ions becomes equal to one another—*i. e.*, equal to the concentration in the medium itself. As a consequence, although at comparatively great distances from the particle (say, of the order $1 \cdot 0 \mu = 10^{-4}$ cm.) the electrical force due to the particle is zero, and, consequently, two particles separated by such distances have no mutual repulsion, whenever two particles do approach one another more nearly they will mutually repel with a force which increases rapidly as the distance apart decreases. This explains why "union does not take place under normal conditions." There remains the question, "Why does the addition of electrolytes allow particles to come together"? In connexion with the effect of added electrolytes on the disposition of ions in the outer Helmholtz layer, Gouy proves (1) that, as the concentration of the ions of given valency is increased, the distance of the centre of gravity of the outer layer decreases, (2) that, for given concentration, ions of uni-, di-, tri-, etc., valency will give progressively thinner outer layers, the effect of the valency increasing exponentially with increasing valencies, and (3) that for liquids very slightly ionized the outer layer occupies a considerable thickness, many microns for pure water and still more for other liquids.

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* Svedberg, 'Colloidal Chemistry' (Chem. Cat. Co.), p. 102.

† Porter and Hedges, Trans. Far. Soc. xviii. pp. 1–9, see p. 6.

‡ Smoluchowski, *Zeit. f. Phys. Chem.* xcii. p. 129 (1917).

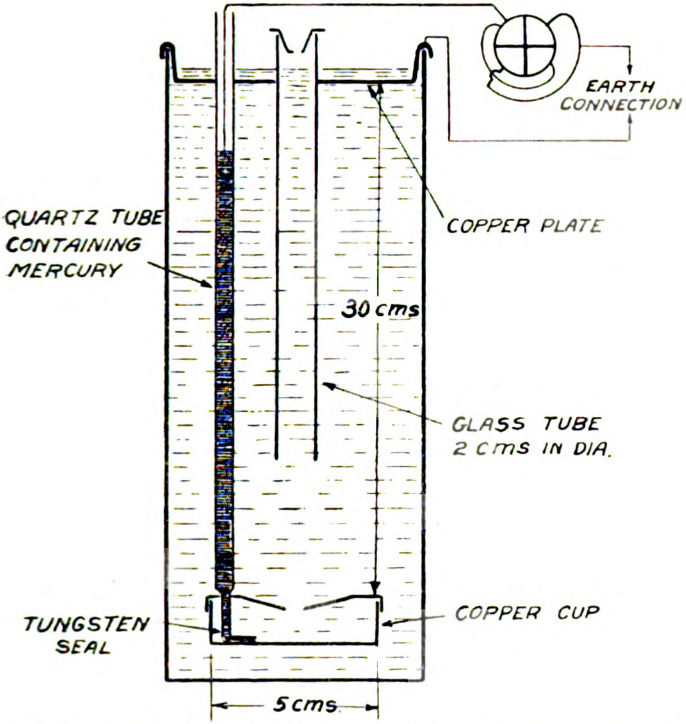
In view of these results we may construct a complete picture of the mechanism by which added electrolytes bring about coalescence, and, also, gain an insight into the abnormal effect of ions of different valencies. Let us replace Smoluchowski's assumptions given above by the following: (1) Particles on near enough approach to one another are drawn together by capillary action; (2) that "union does not take place under normal conditions" is accounted for by the mutual repulsion of the particles due to an effective charge, which becomes active when the particles approach one another within the limits of the diffuse Helmholtz outer layer; (3) added electrolytes, by suppressing the diffuseness of this outer layer, reduce the effective distance at which the repulsive force comes into play; and, finally (4), by a discharge of the particle, the electrolytes destroy the source of the force which kept the particles apart.

The continuous Brownian movement will tend constantly to cause the particles to collide with one another. While the electrical charge is large enough, mutual repulsion will prevent the particles from approaching one another nearer than a certain distance. If, by the addition of electrolytes, the particles are discharged, which is an experimental fact, then that mutual repulsion which has prevented collisions is wiped out. Following this out, Gouy's results lead also to a very logical explanation of the curious valency relation existing among ions producing coagulation, known as the Schulze-Linder-Picton law.

IV. *Experimental Work: Mutual Repulsion of Large Like-charged Spheres falling through Liquids.*

(1) *The Charge on Particles.*—The purpose of the following experiments was to find whether charged particles of macroscopic size moving through liquids could be shown to exert a mutual repulsive effect. As a source of charged particles, advantage was taken of a phenomenon first reported by Dorn (4), viz., that particles of metals, powdered quartz, etc., in falling through a column of water, carry a negative charge and thus tend to set up a difference of potential between the top of the column and the bottom.

Fig. 2.



These experiments have been repeated and extended using water and other liquids; the collected results are shown in Table II. The apparatus used is shown in fig. 2. A weighed amount of lead shot (pellets about 1 mm. in diameter) was let fall through a column of liquid and caught at the bottom in a copper cup which was almost entirely closed and joined by means of metallic connexion through a quartz tube with a pair of quadrants of a Dolazelek electrometer. Just below the surface of the liquid in the column an earth-connected copper plate was placed, so that readings on the quadrant electrometer gave an indication of the potential difference set up between the copper plate and the copper cup—or, in other words, a measurement directly proportional to the charge carried down by the lead spheres. Most of the experiments were carried out with water of low conductivity and various other (organic) liquids which invariably had very low conductivity. In carrying out a single observation, the copper cup and its quadrant were isolated by breaking their temporary earth connexion; the needle of the electrometer would then move so as to indicate a very small difference of potential between the copper cup and the upper copper plate; this small deflexion was in any case quite steady. A weighed amount of lead shot was then dropped into the central tube and, of course, fell quickly to the cup. At the instant the lead struck the cup, the electrometer needle swung out, in those cases giving any such effect at all. Central tubes of different lengths were tried, with but little variation shown in the results; consequently, such a length was chosen as to assure that all the shot was caught in the lower cup. Various lengths of liquid columns were tried, and when the distance between the top and bottom electrodes reached some 15 or 20 cm. the results remained constant; a convenient length of about 30 cm. was chosen.

TABLE II.

Liquid.	Sign of Charge.	Size of Charge.
Water	—	Large.
Alcohol	—	Very small
Benzene	—	Very large.
Toluene	—	Very large.
Xylene	—	Very large.
Turpentine	+	Very large.
Carbon tetrachloride.	+	Small.
Chloroform	No	
Ether	No	
Acetone	No	
Aniline..................	No	

It will be noticed that benzene, toluene, and xylene give large deflexions showing negative charges carried down, water apparently not so large negative, while turpentine and carbon tetrachloride give positively charged particles (see Wiedemann, 1). It is, of course, apparent that the deflexion of the electrometer will depend on the rate of leak of electricity through the liquid column, so that the deflexion obtained is not an exact measure of the charge carried down by the particles; for a given charge, the deflexion will be greater, the better the insulating properties of the liquid column.

In Table III. are shown the typical results obtained from using increasing weights of shot with the same liquid column. It is apparent that the effect increases with increasing numbers of shot, and we may conclude that each particle of shot carries with it a definite charge.

Table III.

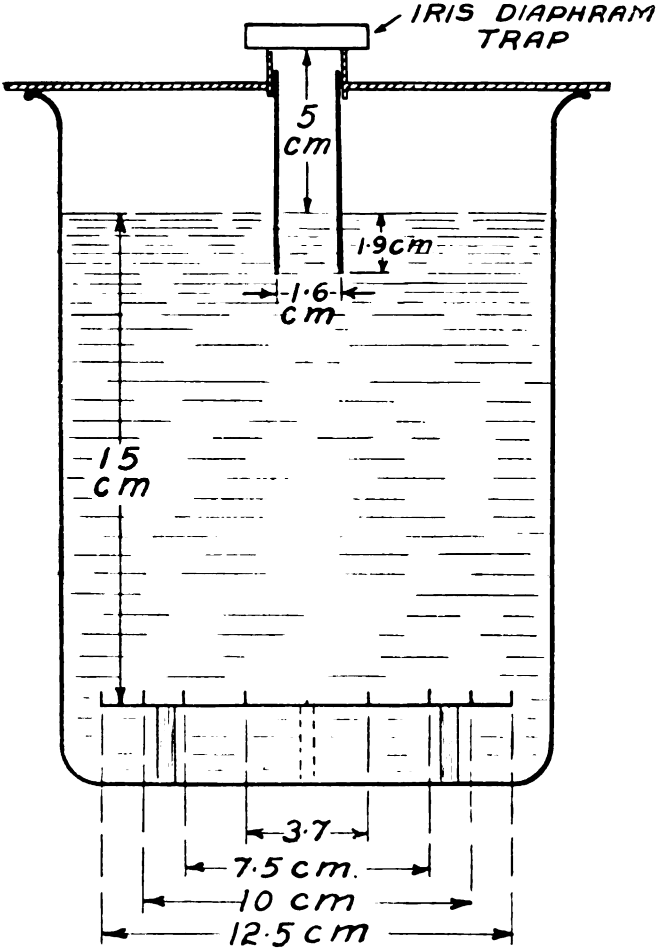
Weight of Shot.	Electrometer Deflexion.
2 gms.	2·25
4 „	4·25
6 „	4·85
10 „	7·45
12 „	8·10

This phase of the work has not as yet been followed sufficiently to enable one to make a definite announcement of the charge per shot. For the present purpose, we have established that for some media these lead spheres become negatively charged, for others positively charged, while in still other cases there is no indication of a charge at all.

(2) *Effect of Charges on the Scattering of a Cloud of Particles in falling through Liquids.*—If a small cloud of particles such as the lead spheres used above is dropped through a short funnel into a column of liquid, one can easily observe considerable spreading taking place during the descent. Rough preliminary experiments on this phenomenon gave distinct indications that, in cases where the electric charge was large, the spreading was large. Apparatus was devised to attempt to measure the amount of spreading or scattering of the shot on falling through a definite distance in various liquids; measurements have been made whereby a "coefficient of scattering" may be determined.

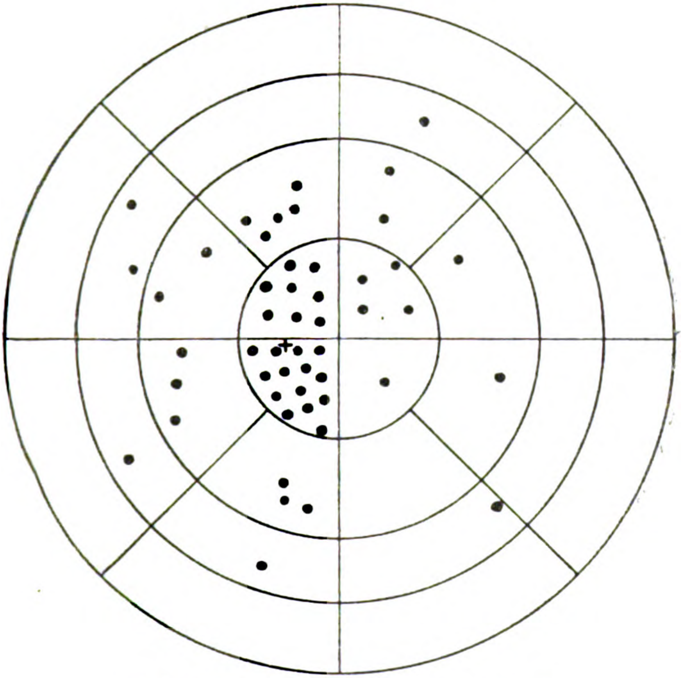
We are, of course, dealing here with a very complex phenomenon ; the scattering will undoubtedly be affected by hydrodynamic forces due to the spheres moving in parallel paths through a viscous liquid, by possible momentary abrupt gradients of temperature in the column, by collisions, and so on. However, certain experiments have been made to determine such disturbing features, and definite indications of the scattering due to electrical charges have been found.

Fig. 3.



The apparatus for determining scattering is shown diagrammatically in fig. 3 ; it represents the final form after many attempts. For any one observation fifty pieces of shot of fairly uniform size were released simultaneously by a photographic shutter arranged as a trap at the top of a short glass tube kept centrally placed over a vessel of the liquid to be tried. The shot fell a distance of about 5 cm. before striking the liquid, and left the glass tube at a distance of some 2 cm. below the surface. As soon as they leave the tube scattering occurs. At a fixed distance, 15 cm., below the liquid surface, a flat metal pan, subdivided as indicated in fig. 4, served to catch the pieces of shot and retain them practically at the points at which they struck. This pan, which was lined with filter paper, covered the whole cross-section of the beaker containing the liquid, and so would account for every one of the spheres. As the liquids were transparent the shot positions could be recorded on a plan of the pan (fig. 4).

Fig. 4.



PARTICLES CAUGHT IN TRAY.

The radius of the inner circle, which is divided into four quadrants was ·75 in.* ; as, usually, a rather large number of the shot fell in the central part, those in each of the central sections were evenly disposed over each of these sections in the plan made; for all other shot the exact relative position was recorded on the plan. Fig. 4 is a fair sample of what was obtained in hundreds of cases plotted. As is indicated in this figure, it often happened that the centre of greatest density was slightly displaced from the centre of the pan, and consequently in each case a new plan was produced by erasing the bounding lines (fig. 4), selecting a centre of maximum density (marked with a +) and, with this point as centre, drawing a series of concentric circles of 0·5, 1, 1·5, 2·0, 2·5 inches in diameter. The ordinary Gauss formula for departure from a mean was used in determining what would be a measure of the amount of scattering—or a "coefficient of scattering" (S), as it may be called; this formula is as follows:—

$$S=0{\cdot}6745\sqrt{\frac{\Sigma xr^2}{N-1}},$$

where x particles are at a distance r from the centre and N = the total number of particles $=\Sigma x$.

For example, in fig. 5, those within the inner circle are taken to be, on the average, 0·25 in. from the centre, those in the next zone average 0·75 in. from the centre, in the next 1·25 in., then 1·75 in., and so on.

From the distribution shown in fig. 5, the coefficient of scattering works out as follows:

$$\Sigma xr^2=\left\{\begin{array}{l} 16\times\ {\cdot}0625=\ 1{\cdot}00 \\ 18\times\ {\cdot}5625=10{\cdot}13 \\ 11\times 1{\cdot}5625=17{\cdot}19 \\ \ 5\times 3{\cdot}0625=15{\cdot}31 \end{array}\right\}=43{\cdot}63.$$

Since $N=50$, we find $S={\cdot}629$.

On account of the large quantities of liquids necessary to perform the scattering experiments, only the cheaper, more easily obtained liquids were used for this determination; at the same time, an attempt was made to cover a wide range of properties in the liquids chosen. In every case, the scattering coefficient given is the mean value of at least six determinations, and may be considered as reasonably reproducible. The results are given in Table IV., in which are recorded the viscosities and certain other calculated scattering coefficients referred to later.

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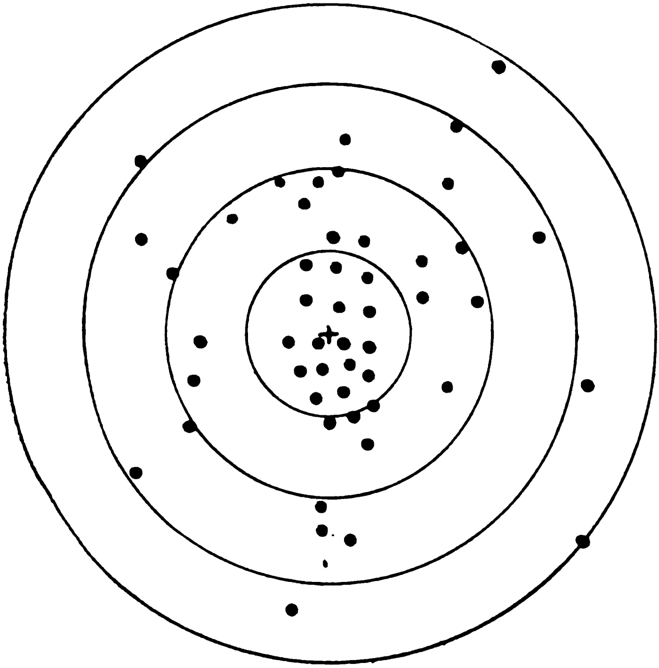
* The inch was used in construction of the pan, and hundreds of calculations were made in this unit; as the resulting numbers are, in any case, merely arbitrary, the change to cm. has not been made.

Fig. 5.



CALIBRATION OF DISTRIBUTION.

Table IV.

Influence of Viscosity of Medium on Scattering.

Liquid.	Coefficient of viscosity at 10° C.	Viscosity in relation to water as unity.	Scattering coefficient calculated from viscosity curve.	Actual value of scattering coefficient.	Charged?	% Difference.
Water	·0131	1·00	·580	—	Yes	—
Turpentine ...	·0178	1·36	·510	·555	Yes	+8·8 %
Ethyl alcohol.	·0145	1·10	·565	·582	Yes	+ 3 %
Ether	·0026	0·20	·750	·620	No	− 17 %
Benzene	·0076	0·58	·670	·686	Yes	+2·4 %

As noted above, there must be many influences affecting the amount of scattering ; whatever the influences may be, they would involve in an intimate manner the viscosity of the liquid. In order to test the effect of viscosity, a series of aqueous sugar solutions of varying concentrations were prepared and their scattering coefficients determined. Table V. shows these results, which are illustrated in the curve of fig. 6.

TABLE V.

Scattering Coefficient of Aqueous Sugar Solutions.

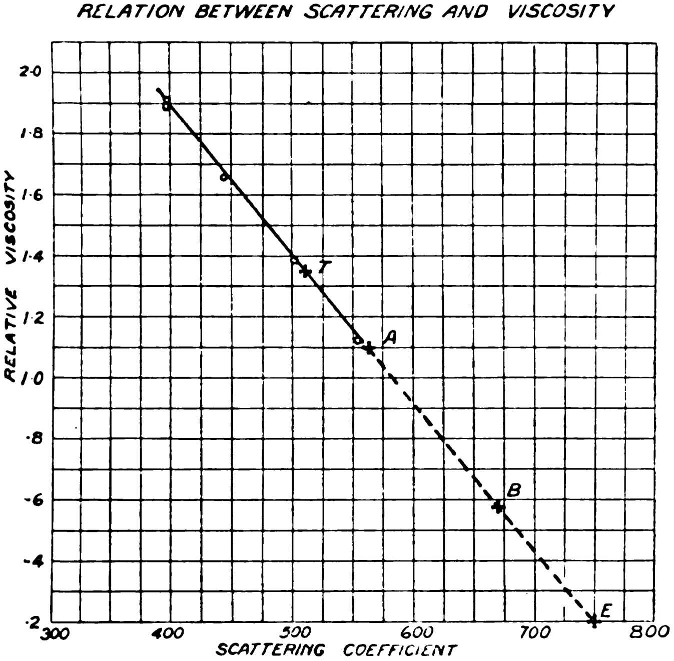
Viscosity.	Specific conductivity.	Scattering coefficient.
Water taken as 1.		
1·127	$6{\cdot}7 \times 10^{-6}$	·559
1·385	$2{\cdot}1 \times 10^{-5}$	·507
1·603	$2{\cdot}5 \times 10^{-5}$	·444
1·885	$2{\cdot}7 \times 10^{-5}$	·395
1·913	......	·398

In considering these results it must be borne in mind that viscosity is not the only variable and that a change in conductivity of the solutions may have an effect on the coefficient of scattering. However, the curve shows distinctly that the increase of viscosity cuts down the amount of scattering in a manner almost directly proportional to the viscosity. Judging from this curve, if viscosity were the dominating feature with various liquid media, the coefficients of scattering for the liquids listed in Table V. should be those recorded in column 4 of that Table (points T, A, B, and E in fig. 6). Reference to Table II. will show that those liquids which show a charge produced on the lead spheres have a larger scattering coefficient than sugar solutions. But that liquid which gives absolutely no indication of a charge imparted to the spheres, viz. ether, gives a scattering much less than one would have expected from its very low viscosity. We conclude then that something causing scattering is lacking in the ether but present in the other liquids, and we know that electrical charges are lacking in ether but present in the others.

V. *Conclusions.*

We believe we have recorded above definite experimental evidence of mutual repulsion produced between similarly charged spheres in various liquids. When one calculates the repulsive force which might be expected, one finds that it must be very small, but even a very small force between the particles would be sufficient to show a distinct effect on the scattering coefficient.

Fig. 6.



Summary.

1. Experiments of Dorn and others on the charge carried by solid particles falling through a column of liquid have been repeated and extended to liquids other than water or aqueous solutions.

2. Lead shot dropped through water, alcohol, benzene, toluene, and xylene carry down a negative charge; through turpentine and carbon tetrachloride a positive charge; and through ether, no charge.

3. Distinct evidence of a scattering due to the possession of a charge has been found, showing that there is undoubtedly a mutual repulsion existing between the particles of shot.

Department of Physics,
University of Toronto.

XXIII. *The J-Phenomena and the Quantum-Theory of Scattering of X-radiation.* *By* R. T. DUNBAR, *Ph.D., University of Edinburgh* [*].

Introductory.

WHEN X-rays pass through matter it is observed that the intensity of the transmitted X-rays, as measured by ionization or other process, is less than the incident intensity, showing that the radiation loses energy. The loss, however, in certain cases has been found to be completely accounted for by the appearance of three secondary radiations, the energy thus emitted being within the error of experiment equal to the energy lost in the process of absorption. The theory of the latter process has been arrived at by detailed examination of the secondary radiations, namely, (1) the "scattered" radiation, (2) the "corpuscular" radiation, or emission of electrons, and (3) the "fluorescent" X-radiation, and it accounts for these, as is well known, by assuming two simultaneous but totally different and independent types of absorption. The incident radiation does work on each electron it passes over, the electric vector producing an acceleration, or more definitely, a forced vibration which conforms with the classical laws of electrodynamics. The energy thus absorbed is re-radiated by the electrons, again according to the classical laws. The other process of absorption is that which we associate with the photo-electric effect. We know nothing of the actual process of absorption but can account for its effects by the assumption of certain empirical laws. The theory is that only those electrons which require less energy to remove them from their atoms than a quantum of the incident radiation can take part in this absorption. The chance that an electron satisfying this condition will absorb energy is almost infinitesimal, and is a function of the energy-level of the electron, of the energy quantum of the incident radiation, and of the atomic number of the element. The energy absorbed by one electron is a single quantum of the incident radiation: part of this energy is required to remove the electron from its atom, and the remainder appears as kinetic energy. Taking this fact in conjunction with the above law, we see that an electron must be ejected for every quantum of energy absorbed. The replacement of electrons thus removed gives rise to X-radiation characteristic of the element. Thus we account for the secondary corpuscular and fluorescent X-radiations.

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[*] Communicated by Prof. C. G. Barkla, F.R.S.

The theory outlined above is very substantially supported by a comprehensive and detailed examination of the phenomena which accompany the absorption of X-radiation. In particular, the scattered radiation has been found * to have the same penetrating power as the absorbed radiation, and its intensity, distribution, and polarization have been shown to be exactly that which the theory would predict. The evidence is so complete, in fact, that there can be no doubt that the true explanation of the origin of the scattered radiation, in the case of X-rays of long and medium wave-lengths at least, does not differ fundamentally from that which has been given.

Recent experiments by A. H. Compton and others on the scattering of monochromatic radiations of short wave-length by light substances have demonstrated, however, that the process of scattering under certain circumstances must undergo a radical change as the wave-length is reduced below a certain value. Compton † has shown (and his results have been confirmed by numerous other experimenters) that the bulk of the scattered radiation from certain light substances may differ in wave-length from the absorbed radiation, the wave-length being greater in the case of the scattered radiation by $0{\cdot}0242\ (1-\cos\theta)$ Å, where θ is the angle between the primary radiation and the direction of scattering. The quantum-theory of scattering which Compton ‡ has put forward to account for his results and for the results obtained by various experimenters on the absorption of γ-rays, in spite of its apparently highly improbable assumptions, has succeeded in accounting remarkably well for the observed phenomena in the region of short wave-lengths. If we accept Compton's theory as a possible process of scattering §, we are led to certain interesting and important considerations. To explain the phenomena of polarization, the reflexion, without change of wave-length, of X-rays by crystals and the presence of a certain intensity of untransformed scattered radiation in Compton's experiments, we are compelled to accept the classical theory as also a possible process of scattering. We have now two possible processes of scattering, and which of the two will be

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* Barkla, Bakerian Lecture, 1916.

† A. H. Compton, Phys. Rev. xxi. .p. 483 (1923).

‡ A. H. Compton, *loc. cit.*

§ The application of the term "scattering" to a new process is open to criticism, but in the present paper it should give rise to no ambiguity.

effective must be determined by the conditions of experiment. That there really are two alternative processes seems to be indicated by the fact that experimenters, presumably working under slightly different, though in some cases apparently identical conditions, have obtained results which are clearly inconsistent with one another. Clark and Duane [*] in attempting to reproduce Compton's results in analysing the radiation scattered by various substances with a highly refined X-ray spectrometer, found that the radiation was unchanged in wave-length. Barkla and Sale [†], on comparing the qualities of the primary and secondary rays in the case of paper with heterogeneous rays over a long range of penetrating powers, found at the softer end of the range that the qualities were identical, while at the harder end the qualities were sometimes found to be alike and sometimes to differ by an amount which was considerably greater than that calculated on the theory of Compton. (With heterogeneous rays we have to consider, of course, the possibility of unequal scattering of the constituents which in itself would cause a difference in penetrating power of the beam as a whole.) Assuming, then, the possibility of both processes of scattering and that the condition which decides which process is to be operative depends on some other factor than the wave-length, then for the case of an observer who found the radiation unchanged in wave-length we simply suppose the conditions were not favourable for the quantum process. If we supposed it possible under certain conditions for both processes to be effective simultaneously, an increase in the absorption-coefficient would appear, and this at first sight seems to suggest a solution of the elusive and still unexplained J-absorption phenomena of Barkla. The most important aspect of the present state of the theory of scattering is that we have, or seem to have, a classical process giving place to a quantum process under conditions which have not yet been defined. The discovery of these conditions may well be the first step towards the solution of the more general problem, namely, the process underlying the quantum theory of radiation in general.

When we come to consider what the controlling conditions may be, we are confronted with an enormous number of possibilities. One primary radiation may differ from another in total intensity, in the intensity distribution with reference to wave-length, in polarization, and possibly in other ways which we are as yet unable to define. Radiators may differ in the degree and the orientation of their crystallization, the strong electrostatic field in the neighbourhood of the X-ray tube may have some influence on the interaction of the X-rays with the material of the radiator, if the latter is an imperfect conductor and is not shielded. There is little to be gained by enumerating possibilities. A solution of the problem should be arrived at most quickly by comparing the conditions obtaining in experiments which gave inconsistent results.

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[*] Clarke and Duane, P. N. A. S. Mar. 1924.

[†] Barkla and Sale, Phil. Mag. April 1923.

The experiments described below on the absorption of X-rays and on the corpuscular emissions from gases and solids under the action of X-rays were carried out some time ago. Their purpose was to confirm and extend the evidence for the J-discontinuities which had been obtained by previous experimenters in this laboratory. The J-discontinuities did not appear, although others had obtained irregularities of the order of 50 per cent. and more in some cases, irregularities which could not reasonably be accounted for by experimental error or imperfect apparatus. Experiments on the J-discontinuities have therefore produced the same kind of inconsistencies in the same region of the X-ray spectrum as those on the quality of the scattered radiation, and it is natural to suppose that the two phenomena are connected and that the solution of one will provide also the solution of the other. The scattering experiment described at the end of this paper, when taken in conjunction with the results of the absorption and corpuscular experiments, furnishes a good deal of evidence in favour of the quantum theory of scattering. Some attention has been given to the description of the experimental conditions so that these may be available for comparison with those of experiments which gave different results.

Experiments.

The source of X-rays in all the following experiments was a Coolidge tube of the "broad-focus" type with tungsten anticathode. The general radiation from this tube was filtered down with absorbing sheets of aluminium (and sometimes copper) so as to obtain a fairly homogeneous "end-radiation." The thickness of the filter has in all cases been entered in the tables of observations. The source of high-tension current was a "Mammoth" 16 in. coil operated by a "Sanax" mercury break, the primary current being obtained from the City Supply at 230 volts.

I. *Absorption Experiments.*

When a beam of homogeneous rays of intensity I_0 passes through a thickness x of a substance of density ρ, the transmitted intensity I is given by the well-known absorption formula,

$$I = I_0 e^{-\mu x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where μ is a constant which depends on the wave-length of the radiation and on the absorbing substance, and is independent of the thickness x. μ is called the absorption-coefficient and μ/ρ the mass-absorption coefficient for the absorbing substance for the radiation of that frequency. When the radiation is heterogeneous the value obtained for μ is found to diminish with increasing thickness x, for the less penetrating constituents of the radiation are reduced more rapidly in intensity as the radiation traverses successive layers of the absorbing substance. If x is always adjusted so as to reduce the incident intensity to 50 per cent., the resulting value of μ will give what we may call an average absorption coefficient. The values of μ/ρ in the present absorption experiments were found to vary little with x, showing that the filtered radiation was fairly homogeneous. This allowed considerable latitude in the percentage absorbed. The percentages actually absorbed have been entered in the tables of observations.

The mass-absorption coefficients for silver, aluminium, and paper were compared with those for copper over a range of wave-lengths which included those at which appeared the J-discontinuities of Barkla and White[*]. The apparatus was arranged as in fig. 1, with slight modification. Three electroscopes of the Wilson cubical type were set up in front of apertures, so that a pencil of radiation was directed into each. In reality a number of pencils were arranged to enter each so as to ensure a fairly uniform distribution of ionization, and thus reduce the chance of recombination. Filtering sheets of copper and aluminium were placed against the apertures in the lead box *a*, *b*, and *c*, on the side remote from the tube. Their number was increased or diminished so as to give as homogeneous an end-radiation as possible, consistent with a reasonable transmitted intensity. Stray lead L-radiation from the inside of the box was effectively prevented from reaching the electroscopes by the lead cylindrical tubes placed immediately behind the apertures, as shown in the figure. A range of wave-lengths was obtained by adjustments of the primary current of the induction-coil, and the intensity was controlled by modifying the temperature of the cathode. The relative rate of leak of the electroscopes when identical filters were placed in front of the apertures was found to vary slightly with wave-length, but this was taken into account. Absorption sheets of copper and other substance were added to the filters at *b* and *c*, respectively. Their thicknesses were adjusted to reduce the rates of leak of the corresponding electroscopes to about half, the third electroscope being used as a standard. The values of the mass-absorption coefficients for the two substances were calculated from equation (1), the rate of leak of an electroscope relative to that of the standard being taken as a measure of the intensity transmitted towards that electroscope. The results of the observations are given in Tables I., II., and III. Plotting the values of μ/ρ for silver, aluminium, and paper against μ/ρ for copper (Graph I.), we

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[*] Barkla and White, Phil. Mag. Oct. 1917.

Fig. 1.

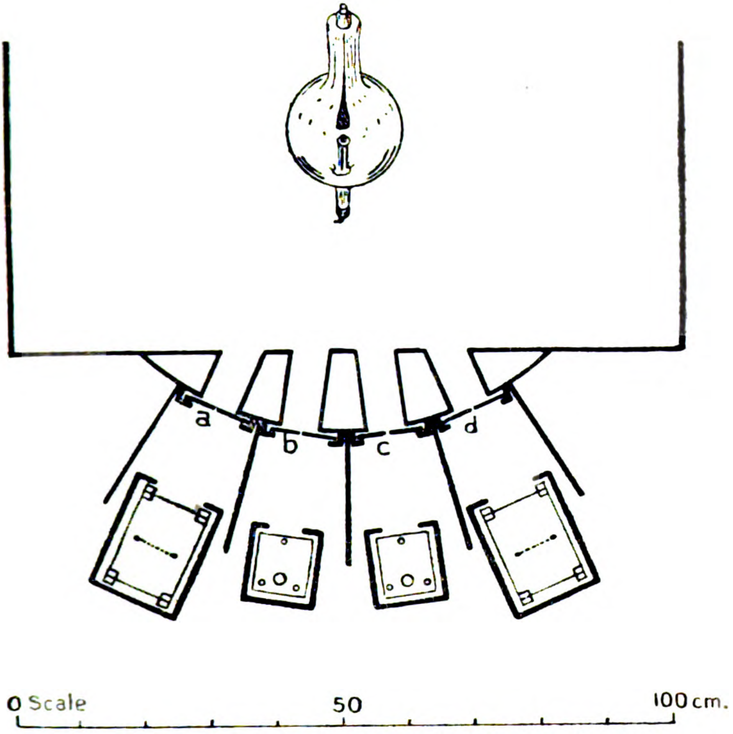


Table I.—Mass-absorption coefficients for Silver and Copper.

Filter.	Per cent. absorption by Ag.	Per cent. absorption by Cu.	μ/ρ for Ag.	μ/ρ for Cu.
0·2 mm of Cu and 6·5 mm. of Al	55	51	13·65	4·35
	57	53	14·5	4·60
	59	55	15·1	4·81
	59	56	15·25	4·95
	60	57	15·6	5·04
	60	57	15·8	5·10
	61	57	16·05	5·17
	62	59	16·6	5·35
	62	58	16·8	5·32
	63	60	16·9	5·47
	63	59	17·2	5·46
	65	61	17·8	5·78
	65	62	18·2	5·94
	66	62	18·5	5·85
	70	67	20·45	6·75
	46	44	11·38	3·52
	48	46	12·07	3·78
	51	49	13·04	4·10

Table II.—Mass-absorption coefficients for Paper and Copper.

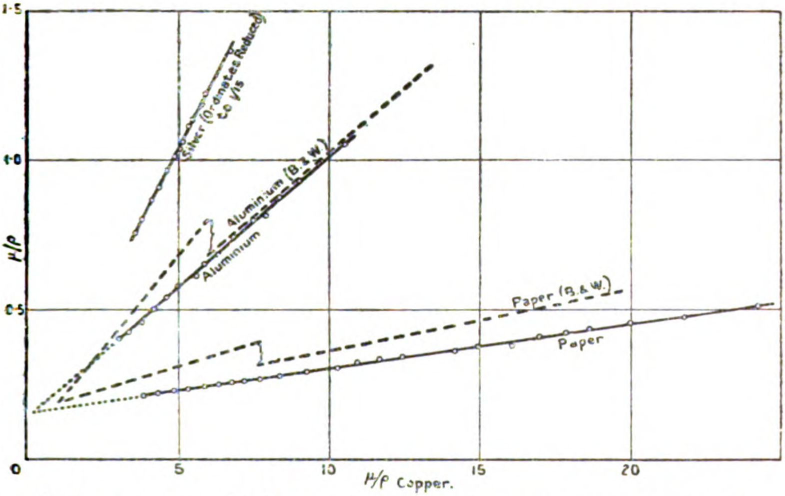
Filter in mm. of Al.	Per cent. absorption by paper.	Per cent. absorption by Cu.	μ/ρ for paper.	μ/ρ for copper.
22·8	46	48	0·218	3·82
...	47	50	0·226	4·30
...	48	56	0·232	4·85
...	49	58	0·239	5·30
18·0	50	62	0·247	5·86
16·3	51	65	0·253	6·32
...	52	68	0·260	6·77
...	52	64	0·265	7·18
13·0	53	56	0·270	7·69
...	49	42	0·282	8·37
10·7	40	32	0·294	9·28
...	41	35	0·310	10·28
9·8	44	37	0·328	10·95
7·4	44	38	0·330	11·68
6·5	46	40	0·346	12·45
...	47	45	0·365	14·20
...	49	46	0·381	14·95
...	49	50	0·385	16·10
...	49	49	0·412	17·00
4·15	50	53	0·426	17·86
...	48	54	0·440	18·65
...	45	57	0·457	20·00
...	46	60	0·476	21·80
3·25	60	64	0·511	24·27
...	61	66	0·544	26·05
...	62	68	0·562	27·20
nil	54	69	0·583	28·20
3·25	60	72	0·604	30·45

TABLE III.

Mass-absorption coefficients for Aluminium and Copper.

Filter.	Per cent. absorption by Al.	Per cent. absorption by Cu.	μ/ρ for aluminium.	μ/ρ for copper.
0·28 mm. Cu & 16·3 mm. Al	51	47	0·402	3·00
......	52	50	0·426	3·33
......	56	55	0·460	3·78
0·28 mm. Cu & 13·0 mm. Al	59	58	0·504	4·175
......	62	69	0·542	4·60
0·28 mm. Cu & 9·8 mm. Al	64	65	0·578	4·98
......	66	69	0·618	5·59
......	52	52	0·655	5·86
......	70	74	0·686	6·32
......	57	58	0·747	6·83
0·28 mm. Cu & 6·5 mm. Al	60	61	0·802	7·49
0·28 mm. Cu & 3·25 mm. Al	52	48	0·818	7·90
......	58	58	0·878	8·37
......	56	53	0·933	9·00
......	60	59	1·052	10·52

Graph I.



find no trace of discontinuities. An examination of the results will show that, by allowing a probable experimental error of only 1 per cent. in the determination of μ/ρ all the deviations from a linear relationship between the mass-absorption coefficients can be accounted for. The results obtained by Barkla and White for paper and aluminium are indicated by broken lines in the same graph. A comparison of the two sets of curves shows conclusively that whatever produced the discontinuities in the one set of curves was certainly not present in the other. Hence we may conclude that under the conditions of experiment described above the J-discontinuities do not appear.

The present experiments differ from those of Barkla and White in the following respects :—

(1) A Coolidge tube was used in place of a gas-filled tube.
(2) The distance between anticathode and filters was about 48 cm., or about 2 or 3 times that in the other case.
(3) The anticathode was of tungsten in place of platinum.
(4) The filters were thicker in the experiments now described, about 2 to 4 times as thick in the regions of the discontinuities, so that the end-radiation was very probably more homogeneous.

II. *Experiments on Corpuscular Radiation.*

The intensity of the corpuscular radiation from a substance exposed to the action of X-rays may be conveniently measured, if the substance is in the form of a gas, by finding the intensity of ionization produced by the complete absorption of the corpuscles by the gas itself. If the substance is in the form of a solid, a plate of the substance may be exposed, in an atmosphere of hydrogen, to the action of the X-rays, when the ionization of the hydrogen will be produced almost entirely (over 99 per cent. probably) by the corpuscles sent out from the plate. The intensity of ionization of the hydrogen will afford a measure of the intensity of the corpuscular emission from the substance of the plate. This method of measurement is evidently suitable for the location of discontinuities. These two methods of studying the intensities of the corpuscular emissions were applied to various substances.

The same ionization-chamber was used throughout the experiments. It consisted of a brass cylindrical tube, 14 cm. long and 10 cm. in diameter. The inside of this tube was covered with aluminium foil, and aluminium plates 1·5 mm. thick were fitted to the ends. The electrode was connected to a Wilson electroscope of the cubical type placed immediately under the ionization-chamber. The necessity for taking into account the loss of corpuscles at the sides, and the loss and gain at the ends of an ionization-chamber, and the method of correcting for these by taking ionization-pressure curves are sufficiently well known and need not be considered here. For the present purpose the correction for boundary effects was considered unnecessary, the J-effects being much more discontinuous and of a much greater magnitude than the effects produced by loss and gain of corpuscles at the walls of the chamber.

The apparatus was set up as in the previous experiments (see fig. 1). The ionization-chamber on the left was normally not in use. It was used later to make a direct comparison between pairs of substances where an indirect comparison in terms of a standard electroscope was not considered sufficiently conclusive. One electroscope was used as a standard, the other to measure μ/ρ for the incident radiation, aluminium being used as absorbing substance. The two gases whose ionizations were compared with that of air were sulphur dioxide and ethyl bromide. The ends of the two electroscopes and of the ionization-chamber were covered on the inside with five layers of filter-paper, and precautions were taken to ensure that the radiation was in no case incident on the electrodes. The three gases, air, sulphur dioxide, and ethyl bromide, were introduced in turn into the ionization-chamber, and at least one complete set of observations over a considerable range of wave-lengths was taken with each gas. The ratio of ionization in the chamber, when filled with air, to that in the standard electroscope was found to be constant to about one per cent. over the whole range, from which it was concluded that the difference in the qualities of the pencils of radiation entering the standard electroscope and the ionization-chamber was negligible. In the case of SO_2 several sets of observations were taken, the conditions being altered slightly from set to set. Well-filtered radiation was tried, and a set was taken with the filtering much reduced. The readings were necessarily rough, for reasons that need not be entered into, the accuracy being of the order of about three or four per cent.; but this degree of accuracy would have been ample to show the presence of the J-effect had it been present to only 15 per cent. of its value in the experiments in which it had previously appeared. Table IV. gives the results obtained when the radiation was not highly filtered. In Barkla's experiments, with diminishing wavelength the ratio $\frac{\text{Ionization of } SO_2}{\text{Ionization of Air}}$ decreased suddenly and later increased suddenly to its original value, and the explanation given was that the corpuscular emision from air increased in association with a J-absorption, and, at a shorter

TABLE IV.

Relative Ionizations of Sulphur Dioxide and Air.

Filter in mm. of Al.	μ/ρ (Al).	Per cent. absorbed by Al.	$\frac{SO_2}{Air}$ (observed).	$\frac{SO_2}{Air}$ (corrected) *.
9·8	0·60	41	0·923	0·932
...	0·727	47	0·978	0·991
..	0·92	55	0·994	1·012
3·25	1·53	54	1·007	1·041
nil	4·45	69	0·847	0·966
nil	4·0	65	0·853	0·951
9·8	0·792	50	0·986	1·001
1·5	2·22	44	0·929	0·976
...	2·42	47	0·912	0·962
...	2·60	49	0·908	0·967
nil	4·1	41	0·853	0·955
3·25	1·48	53	1·009	1·041
...	1·63	56	0·995	1·031
...	1·81	60	0·994	1·034
...	1·64	56	1·005	1·041
4·75	1·13	44	1·011	1·036
...	1·24	47	1·014	1·043
...	1·36	50	1·014	1·044

* The ratios in the 4th column are given on an arbitrary scale. The 5th column gives the same ratios corrected for the fact that the X-rays fall off in intensity as they pass through the gas.

wave-length, that from SO_2 increased also by the same fraction. No such effect was observed in the present experiments. The results are plotted with the frequency of the incident radiation as abscissæ, which makes the results simpler of interpretation than when the ratios are plotted against μ/ρ, as will appear. To convert values of μ/ρ for Al to frequencies, it was not considered advisable to use experimental values of the absorption-coefficients of wave-lengths, for these contain experimental errors of appreciable magnitude, judging by the difference between the results of different observers. The probability is that, apart from the regions which contain spectral lines, there exists a smooth relationship between wave-length and absorption-coefficient. An approximate empirical formula (that of Kossel, Siegbahn, and Glocker), founded on experimental values determined up to a recent date, was used, namely,

$$\mu/\rho = 0{\cdot}2 + 0{\cdot}0195\, N^{2{\cdot}58}\, \lambda^{2{\cdot}8},$$

where N is the atomic number of the absorbing element, and λ is the wave-length. This formula is only roughly approximate in the case of Al, but points where irregularities appear can have their true frequency or wave-length determined afterwards, if necessary, by reference to experimentally determined values of the absorption-coefficients of definite wave-lengths.

Graph II. shows the results of the comparison of the ionization of SO_2 and of ethyl bromide with that of air. In the case of ethyl bromide the radiation was well filtered (see Table V.). This substance, owing to its low vapour-pressure, could only be tested at a pressure of a cm. or two of mercury. To prevent excessive loss of corpuscles at the

Graph II.

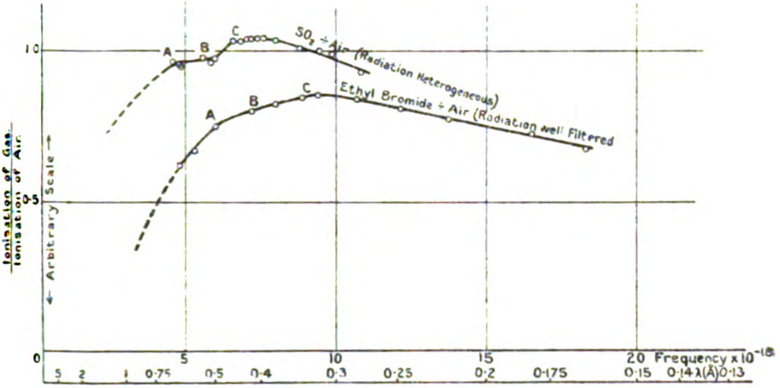


TABLE V.

Relative Ionizations of Ethyl Bromide * and Air.

Filter in mm. of Al.	μ/ρ (Al).	Per cent. absorbed by Al.	$\frac{\text{Eth. Br.}}{\text{Air}}$ (observed).	$\frac{\text{Eth. Br.}}{\text{Air}}$ (corrected) †.
29·3	0·295	54	0·673	0·676
22·8	0·328	51	0·716	0·721
16·3	0·410	51	0·766	0·774
13·0	0·495	50	0·798	0·807
9·8	0·622	50	0·830	0·840
8·0	0·795	51	0·839	0·853
6·5	0·90	55	0·826	0·844
4·65	1·14	52	0·804	0·824
3·25	1·45	53	0·775	0·800
1·40	2·27	43	0·721	0·752
0·47	3·20	55	0·627	0·667
0·00	4·02	43	0·569	0·620

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* The ethyl bromide vapour was mixed with air, but fully 90 per cent. of the ionization was produced by the corpuscular emission from the ethyl bromide.

† This column is obtained as explained in footnote to previous table.

walls of the chamber, which would result from the low pressure of the gas, the pressure was brought up to atmospheric by introducing air. The ionization of a mixture of gases is a complex matter, but for our present purpose it is unnecessary to enter into considerations of this kind. Over 90 per cent. of the ionization of the mixture was attributed to corpuscles from ethyl bromide. Corrections were made on the observations for the fact that the intensity of the primary radiation falls off more rapidly when it passes through the heavier gases. A knowledge of the absorption coefficients of the gases enabled the corrections to be applied.

Before interpreting the features of these curves, let us consider what shape of curve theory would lead us to expect. Absorption experiments have shown that in regions not too near characteristic frequencies of either element there exists a linear relationship between the absorption coefficients of any two elements, and that the "true" absorptions by fixed masses of the two elements (that is, total absorptions less the absorptions associated with scattering) are proportional. The ratio of the "true" absorptions by given masses of two gases is therefore independent of the wave-length in regions remote from their spectral lines. But each quantum absorbed gives by theory one corpuscle; therefore the relative numbers of corpuscles emitted is constant. The energy per corpuscle is $h\nu-h\nu_{\mathrm{K}}$, assuming that the corpuscles emerge from the K-level, which most of them do in the present case. Consequently the total energy of the corpuscular emission and therefore the intensity of the ionization is proportional to $\nu-\nu_{\mathrm{K}}$, so that the ratio $\frac{\text{Ionization of Gas}}{\text{Ionization of Air}}$ is proportional to $\frac{\nu-\nu_{\mathrm{K}_g}}{\nu-\nu_{\mathrm{K}_a}}$, and therefore to $1-\frac{\nu_{\mathrm{K}_g}-\nu_{\mathrm{K}_a}}{\nu-\nu_{\mathrm{K}_a}}$, where ν_{K_g} and ν_{K_a} are the K-level frequencies for gas and air respectively. This gives a rectangular hyperbola cutting the frequency axis at ν_{K_g}. The parts of the curves to the left of C agree very well with this theoretical result, within the error of experiment. The small irregularities at B may be real, but are covered by experimental error and need not therefore be discussed. The drop in the values of the ratios to the right of C could be accounted for by (1) an abnormal falling off in the ionizations of the gases SO_2 and ethyl bromide, or (2) an abnormal increase in the ionization of air. This feature of the curves did not receive due attention at the time the experiments were carried out, for, from the location and gradual nature of the irregularity, it was clear that it was not connected with the investigation in hand, namely the J-discontinuities. The application of the method of ionization-pressure curves to eliminate the effects of end-losses would have simplified the interpretation of this irregularity. Part of the effect is certainly due to end-losses, for the elements contained in paper are on the whole much lighter than those contained in the two heavy gases, and, as the radiation becomes more penetrating, the corpuscles have greater velocities and the net loss at the ends becomes more important. From our knowledge of the ranges of corpuscles in gases, however, it seems unlikely that so large a fraction of the corpuscles would reach the walls of the chamber as would be required to reduce the ionization to an extent that would explain the irregularity. It would seem reasonable, therefore, to conclude that these results are not inconsistent with the view (to which we are led by the results of experiments on plates) that when the radiation is reduced in wave-length below about 0·4 Å, the corpuscular emission from *Air* begins to show an abnormal increase in intensity. The fact that the beginning of the irregularity (C) appears at different wave-lengths on the two curves is probably accounted for by the heterogeneity of the radiation in the case of the upper curve, for the more penetrating constituents are present when the absorbability is still comparatively great.

The plates experimented on consisted of (1) paper, (2) aluminium, (3) copper, and (4) lead. The ionization-chamber was the same as that used in the experiments on gases. The aluminium plates, 1·5 mm. thick, were retained at the ends. Several thicknesses of filter-paper were fixed to the inside surfaces of these aluminium plates when paper was the substance under examination. (It should be mentioned that five sheets on each end gave the same results at all wave-lengths as twelve sheets, showing that five sheets of paper were sufficient to prevent corpuscles from the aluminium reaching the gas.) The paper was replaced by copper foil, and later, when lead was being tested, the aluminium plates were covered with paper and lead respectively, the lead being at the back. The ionization of the hydrogen gas in the latter case was due almost entirely to the corpuscles from lead. It seemed desirable to have the substance whose corpuscular radiation was being tested at both ends of the chamber, in order to eliminate errors which would arise from the known unsymmetrical distribution of the corpuscular emission. This was impracticable in the case of lead, which nevertheless gave a curve with the same features as the others, so that the precaution would seem to have been unnecessary. The hydrogen was obtained from a Kipp's apparatus charged with zinc and dilute sulphuric acid. The action of the zinc on the acid was very slow, which would indicate that these substances were fairly pure. The hydrogen was passed through caustic potash, calcium chloride, and cotton-wool, but no other precautions were taken to exclude impurities.

The ionization of the hydrogen by each of the four substances was compared with that in the standard electroscope over a range of wave-lengths. The results are given in Table VI., and the ratios (on an arbitrary scale) are

TABLE VI.

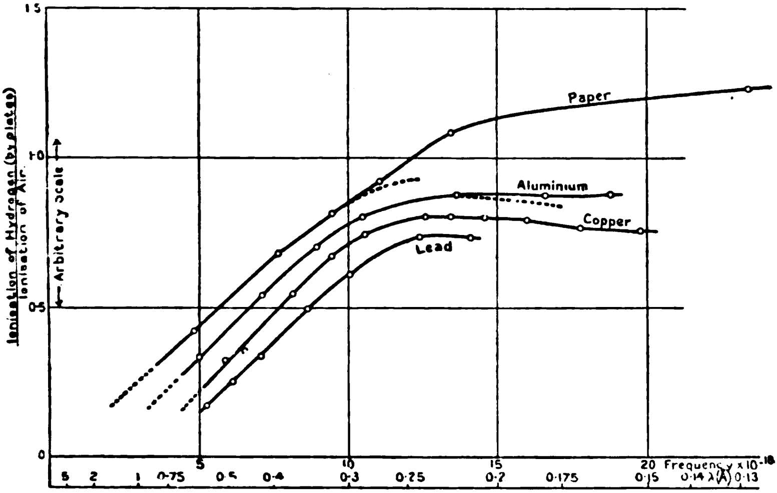
Ionization of Hydrogen by Paper, Aluminium, Copper, and Lead, relative to Ionization of Air.

Filter in mm. of Al.	μ/ρ (Al).	$\frac{\text{Paper}^*}{\text{Air}}$.	$\frac{\text{Aluminium}^*}{\text{Air}}$.	$\frac{\text{Copper}^*}{\text{Air.}}$.	$\frac{\text{Lead}^*}{\text{Air}}$.
29·3	0·244	1·232			
,,	0·275	...	...	0·758	
,,	0·284	...	0·880		
,,	0·300	...	...	0·765	
22·8	0·328	...	0·872		
,,	0·336	...	...	0·792	
19·6	0·376	...	...	0·801	
22·8	0·392	...	...	...	0·736
16·3	0·407	...	0·877		
,,	0·416	1·086	...		
,,	0·422	...	...	0·804	
,,	0·462	...	...	0·804	
,,	0·480	...	...	...	0·736
9·8	0·580	0·925			
,,	0·616	...	...	0·746	
,,	0·635	...	0·803		
,,	0·69	...	...	...	0·610
6·5	0·79	0·812	...	0·672	
,,	0·88	...	0·708		
,,	0·955	...	...	...	0·497
3·25	1·09	...	...	0·548	
,,	1·26	0·683			
,,	1·48	...	0·543		
,,	1·50	...	...	...	0·339
1·40	1·83	...	...	0·358	
,,	2·125	...	...	...	0·252
nil	2·42	...	...	0·321	
,,	3·25	...	...	...	0·172
,,	3·60	...	0·334		
,,	3·97	0·423			

* The ratios are given on an arbitrary scale.

plotted against the frequency of the primary radiation as abscissæ in Graph III. Commencing from the left, the ratios in every case are seen to increase rapidly with diminishing wave-length. This is to be expected for, whereas in the standard electroscope the corpuscles come from a fixed mass of air, in the case of hydrogen the corpuscles come from a thickness of the substance at the ends of the chamber which increases with the initial velocities of emission. The ratio of ionizations is therefore a function of the initial speeds of the corpuscles, that is of $\nu-\nu_K$ in the case of paper, aluminium, and copper, and $\nu-\nu_L$ in the case of lead, approximately. Hence we find that when the

Graph III.



initial straight parts of the curves are produced backwards, the intersection with the frequency axis is approximately at $\nu=\nu_K$ or ν_L, as the case may be. Proceeding to the right, the rates of increase of the ratio with frequency fall off, and the curves become horizontal or nearly so. The energy of the corpuscles is at this stage incompletely absorbed by the hydrogen, the fastest of them from the surfaces of the plates getting right across the chamber without giving up an appreciable fraction of their energy. Ionization-pressure curves showed that even when the radiation was as soft as 3·0 μ/ρ Al, which is near the long wave-length limit of our range, a certain number of the corpuscles were getting across the chamber. Clearly, when the velocities are very great, if we could replace the hydrogen with the substance of the plates in the form of a gas, the pressure being such as to offer the same obstruction to the corpuscles as the hydrogen, the ionization would be the same, for the corpuscles emitted by the gas would reach the walls without giving up an appreciable amount of energy; and this hypothetical arrangement is a chamber of the same kind as the electroscope, in the sense that it contains a gas with ends properly compensated for loss and gain of corpuscles. We would therefore expect that the ratio:

$$\frac{\text{Ionization due to plate}}{\text{Ionization of air}}$$

would approach, asymptotically from below, the ratio:

$$\text{constant} \times \frac{\text{Energy of corpuscular per gram of substance of plate}}{\text{Energy of corpuscular per gram of air}}.$$

The latter, as has already been seen, when the true absorptions of the substances are proportional, gives a rectangular hyperbola of the form:

$$\text{R (Ratio)} = \text{const.} \times \left(1 - \frac{\nu_{K_g} - \nu_{K_a}}{\nu - \nu_{K_a}}\right).$$

The only curve which approximately approaches such an hyperbola asymptotically on the right is that for paper, and this substance has an "average" atomic weight very nearly the same as air. The other substances show a distinct deficiency of ionization at short wave-lengths, the deficiency beginning to be noticeable at about 0·32 Å (see graph). We are led to conclude that the corpuscular emission from air is increasing abnormally with diminishing wave-length, and that the effect begins to be appreciable at 0·32 Å. A comparison of the curves for aluminium and copper shows that the former begins to show an abnormal increase relative to the latter at about 0·215 Å. To check these two results a direct comparison was made between the substances paper and aluminium, and aluminium and copper, using two identical ionization-chambers, placed symmetrically with respect to the tube (see fig. 1). Both irregularities appeared very distinctly. In the case of the comparison of aluminium and copper it appeared, as anticipated, at $\mu/\rho_{\text{Al}} = 0·4$, and attained a value of the order of 10 per cent. when the radiation was hardened to $\mu/\rho_{\text{Al}} = 0·35$. The wave-lengths on the graph were those calculated from an approximate formula connecting absorption-coefficients and wave-lengths. Using the experimental results of Siegbahn and of Hull and Rice instead of this formula, we get the values 0·405 * and 0·275 Å.† for paper and aluminium respectively.

We must now consider this result from the point of view of energy. The mass-absorption coefficients of paper and copper over this region have been shown to be free from irregularities, within a small error of experiment, under apparently identical conditions of experiment (see Graph I.). Now the "true" absorption by paper is transformed almost entirely to corpuscular emission; so that if the total absorption and therefore the true absorption is normal, and the corpuscular radiation increases abnormally when we decrease the wave-length of the incident radiation, the additional energy converted to corpuscular radiation must necessarily come from the absorption associated with scattering—directly, or by a subsequent transformation of the scattered radiation. (It is assumed that no third independent type of absorption exists.) It is here that Compton's theory of scattering comes to our assistance. His theory requires that part of the "scattered" absorption shall give rise to corpuscular radiation. The absorption associated with the latter is given by

$$\sigma_a = \frac{\alpha}{(1+2\alpha)^2} \times \sigma_0,$$

where $\alpha = 0{\cdot}0242/\lambda$, and λ = wave-length of the absorbed radiation in Ångström units, and σ_0 is the value of the scattering coefficient on the classical theory, which is 0·2 × the density of the absorbing substance. The true absorption-coefficients for paper and aluminium for hard X-rays are associated almost entirely with corpuscular emission. The total absorptions associated with corpuscular emission are therefore, according to Compton, approximately proportional to $\bar{\mu}$ (paper) $+\sigma_a$ and $\bar{\mu}$ (Al) $+\sigma_a$ for paper and Al, respectively, $\bar{\mu}$ being the total absorption-coefficient less the total scattering-coefficient. The term σ_a is found, by substituting the known values of $\bar{\mu}$, to add about 8 per cent. and 6 per cent. to the latter at the respective wave-lengths 0·405 and 0·275 Å. for paper and aluminium, and in each case the percentage added has just begun to increase very rapidly. The full effect of the additional corpuscular

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* The radiation was clearly too heterogeneous and the observations too few in number to show separate discontinuities for nitrogen and oxygen.

† It will be noticed that the values 0·32 and 0·215 obtained by applying the formula are considerably in error.

emission would not at first be manifest, for initially the "scattered" corpuscles have only a small speed, and only a thin surface-layer would contribute to the ionization. With shortening wave-length, however, the speeds increase rapidly. This would explain why the actual irregularities at the wave-lengths given are much less than 8 per cent. and 6 per cent.

Further confirmation of this explanation of the irregularities appears on examining the absorption curves in Graph I. more closely. The straight lines drawn through the observations for paper and aluminium intersect at about 0·2 μ/ρ for Cu. According to the classical theory, all three substances should have a value approximating to 0·2 for the mass-absorption coefficient at this point of intersection, the true absorption and the scattered absorption approaching the limiting values 0 and 0·2 times density, respectively, when the wave-length becomes vanishingly small. The values of μ/ρ for paper and aluminium at the point of intersection are both about 0·16. Compton's theory corrects the classical coefficient of scattering by applying the factor $1/(1+2\alpha)$, where α is, as before, $0{\cdot}0242/\lambda$ (Å.). Assuming for the moment that this is right, if we add to the observed values of the mass-absorption coefficient the quantity

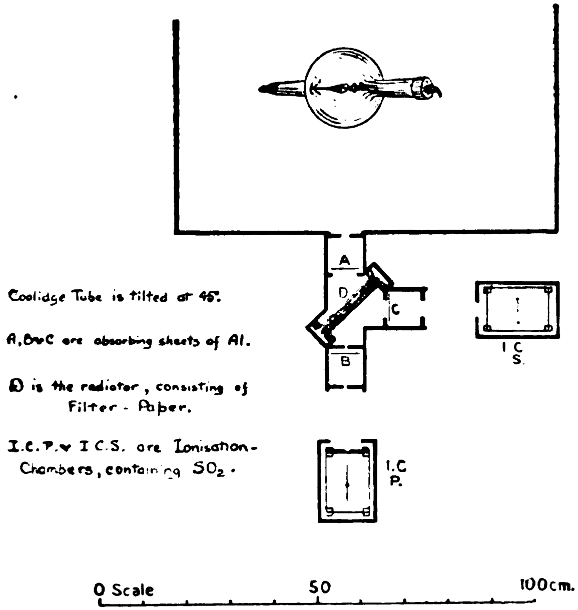
$$0{\cdot}2\left(1-\frac{1}{1+2\alpha}\right),$$

we should obtain the values of the mass-absorption coefficient which would have been obtained had the classical theory been correct. When this is actually done, the new values fall as well upon straight lines as before, but on producing them towards the origin, the three coefficients at the point of intersection are found to be approximately 0·195, 0·195, and 0·2 for paper, aluminium, and copper respectively, and these values are as nearly equal to the classical values as could be expected.

III. *Scattering Experiment.*

We have been led to the conclusion, in discussing the previous experiment, that certain irregularities which appeared might reasonably be explained on Compton's theory of scattering. From this point of view the excess ionization of hydrogen by paper and aluminium when the wave-length is short is to be attributed to the process of scattering, the electrons which scatter the radiation retaining the vector difference between the momenta of the incident and scattered quanta. If this theory is correct, the energy of the excess corpuscular emission must be taken from the "scattered" absorption, only a fraction of the latter reappearing as X-radiation. If it were shown by experiment that the energy scattered as X-radiation was less than the energy absorbed in association with scattering, we should then have qualitative proof that we had correctly traced the origin of the excess corpuscular radiation. The agreement already pointed out between Compton's theory and experiment with regard to the total energy absorbed in the process of scattering, in the case of paper and aluminium, leads us to suppose that Compton's calculated value for the absorbed energy is at least very close to the truth. If, then, we measure the quality and intensity of the scattered radiation in a number of directions over a range of wave-lengths, and compare the results with the values calculated on Compton's theory, agreement between experiment and theory would prove that only part of the energy absorbed in the process of scattering reappears as X-radiation. In the present experiment, observations of the quality and intensity of the radiation scattered by paper at right angles to the primary were taken. The intensity was measured in arbitrary units only, for the intensity at the long wave-length end of the range is known to be correctly given by the classical theory.

Fig. 2.


A
D
C
B
I C
S.
Coolidge Tube is tilted at 45°.
A, B & C are absorbing sheets of Al.
D is the radiator, consisting of Filter-Paper.
I.C.P. & I C.S. are Ionisation-Chambers, containing SO₂.
I.C
P.
0 Scale
50
100cm.

The apparatus is shown in fig. 2. The cathode stream is directed at right angles to the line between anticathode and radiator, but the angle between the cathode stream and the pencil of radiation scattered at right angles into the ionization-chamber was 45° (see figure). This ensured that polarized and unpolarized primary rays would be scattered in the same proportion in the direction of the ionization-chamber. This precaution is obviously essential when the radiation is appreciably heterogeneous, for the constituents of the general radiation from an X-ray tube are not polarized to the same extent. The sheets of filter-paper used as radiator were set up so that their normal bisected the angle between the direction of incidence of the primary and the direction of the secondary scattered pencil, ensuring equal absorption by the radiator of primary and secondary, assuming they differ little in quality.

To measure the intensity of primary and secondary, two ionization-chambers of the same dimensions were used—those, in fact, which were used in the experiments described above. To simplify the interpretation of the results, the same gas was used in both at the same pressure—sulphur dioxide at atmospheric pressure. The windows were of aluminium, 0·1 mm. thick. The primary pencil of radiation entering the chamber was about 0·5 mm., and the secondary about 3 cm. in diameter. Precautions were taken to ensure "saturation," particularly in the case of the primary, where the ionization was produced by a fine intense pencil of radiation in a comparatively large chamber filled with a heavy gas. Care was taken also to prevent incidence of X-radiation on the electrodes.

Diaphragms of lead were placed in such a way as to reduce stray effects (chiefly lead L-radiation) to a minimum. Two were placed between the tube and the radiator, two between the radiator and the primary chamber, and two between the radiator and the secondary chamber. Diaphragms were placed also immediately in front of the windows of the ionization-chambers. All lead close to the radiator was covered with aluminium to absorb tertiary lead L-radiation. A test for stray effect showed that this was small and of the order that would be produced by scattering from the air in the region of the radiator. Filtering-sheets were placed at A (fig. 2) and absorbing-sheets at A, B, and C. The amount of radiation scattered into the chambers by the absorbing-sheets was negligible. The figure is drawn to scale.

Radiators of 268, 50, and 15 sheets of filter-paper were used. The results are shown in Table VII. and Graphs IV.

and V. The mass-absorption coefficients of Secondary and Primary are plotted as ordinates and abscissæ. Compton's theory requires an increase in wave-length on scattering of 0·0242 Å for all wave-lengths scattered at 90°. From a knowledge of relative values of wave-lengths and mass-absorption coefficients for aluminium (approximate values are good enough for the purpose), the theoretical values of μ/ρ_{Al} may be calculated for the secondary radiation. These were calculated, and the differences between the values of μ/ρ_{Al} for secondary and primary were entered alongside the experimental values in the table. Also Compton's theoretical curve is shown by the dotted line in the graphs.

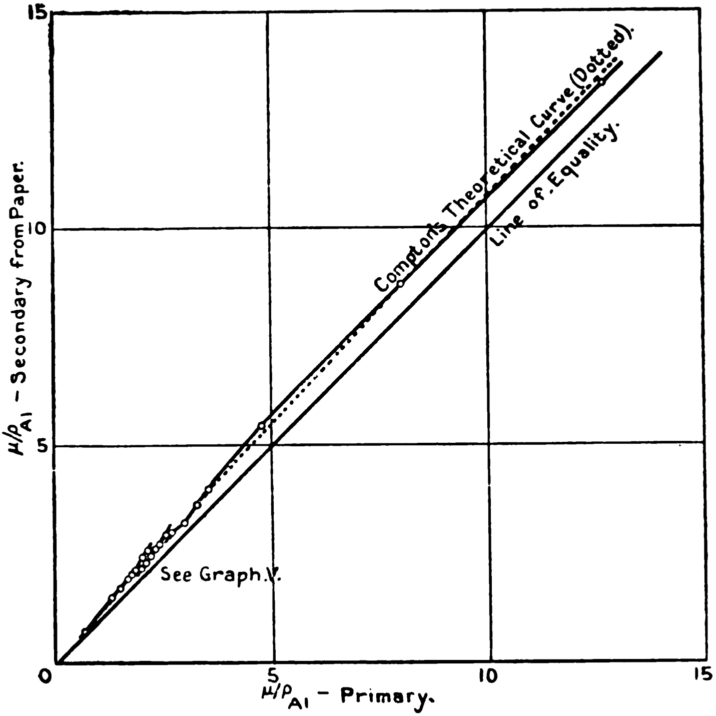
TABLE VII.

Increase ($\delta\mu/\rho$) in μ/ρ on scattering at 90° from Filter-paper.

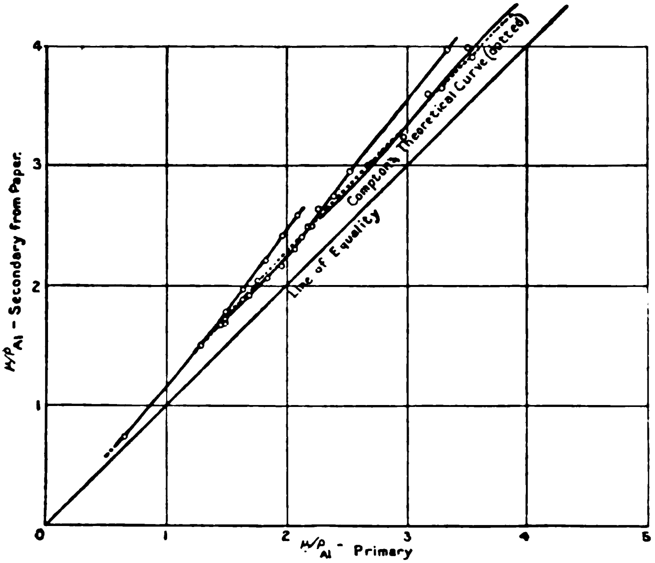
Radiator (filter-paper).	Filter in mm. of Al.	μ/ρ Al. Primary.	$\delta\mu/\rho$. Observed.	$\delta\mu/\rho$. Theory.
268 sheets.	None	2·09	0·50 *	0·27
,,	,,	1·49	0·29	0·21
,,	,,	1·49	0·23	0·21
,,	,,	2·27	0·37	0·28
,,	3·66	0·65	0·092	0·106
50 sheets.	None	3·55	0·36	0·38
,,	,,	3·29	0·37	0·35
,,	,,	4·78	0·65	0·47
,,	0·4	3·34	0·63 *	0·37
,,	,,	3·19	0·41	0·35
,,	0·3	3·51	0·48	0·38
,,	0·6	1·97	0·445 *	0·26
,,	,,	2·31	0·30	0·29
,,	,,	2·40	0·35	0·29
,,	,,	2·20	0·29	0·28
,,	,,	2·13	0·275	0·27
,,	,,	2·18	0·31	0·28
,,	,,	2·08	0·23	0·27
,,	,,	1·96	0·19	0·26
,,	0·92	1·64	0·325*	0·23
,,	,,	1·69	0·23	0·24
,,	,,	1·85	0·21	0·26
,,	1·36	1·30	0·205	0·19
,,	,,	1·48	0·22	0·21
,,	0·5	2·68	0·33	0·31
,,	,,	2·53	0·425 *	0·30
,,	,,	2·98	0·245	0·34
,,	1·36	1·29	0·23	0·19
,,	,,	1·46	0·235	0·21
,,	1·31	1·76	0·285	0·24
,,	,,	1·64	0·245	0·23
,,	,,	1·83	0·38 *	0·26
,,	None	8·03	0·67	0·70
15 sheets.	,,	12·7	0·69	0·90

* These observations are abnormal (see text).

Graph IV.



Graph V.



The observations on the whole are seen to agree fairly well with the theoretical values. The agreement is sufficiently close to conclude that Compton's theory gives the change in wave-length to the correct order of magnitude.

We will now show that the intensity scattered at right angles agrees with the theory. Let λ = the wave-length of the primary, and $\lambda+\delta\lambda$ that of the secondary. According to the theory, $\delta\lambda=0{\cdot}0242$ Å, and, if $\alpha=\delta\lambda/\lambda$, the ratio,

$$\frac{\text{Intensity of Scattered X-radiation}}{\text{Intensity of Primary radiation}},$$

is proportional to $(1+\alpha)/(1+2\alpha)^2$. The distribution of the scattered radiation is nearly the same throughout the region of wave-lengths tested, so that the ratio,

$$\frac{\text{Intensity of radiation scattered at } 90^\circ}{\text{Intensity of Primary radiation}},$$

will also be proportional to this fraction. Now let μ and $\mu+\delta\mu$ be the absorption-coefficients of the primary and secondary for the gas in the ionization-chambers. For a given intensity, the relative absorptions by the gas and therefore the relative ionizations will be given to a sufficiently close degree of accuracy by $(\mu+\delta\mu)/\mu$. The observed values of

$$\frac{\text{Ionization by Secondary}}{\text{Ionization by Primary}}$$

for a range of wave-lengths should therefore be proportional to

$$\frac{1+\alpha}{(1+2\alpha)^2}\times\frac{\mu+\delta\mu}{\mu}.$$

Now μ varies as λ^3, so that $\delta\mu/\mu=3\delta\lambda/\lambda=3\alpha$. It follows at once that to the first order of α (which is 0·08 at most in the present range of wave-lengths, making α^2 about $\frac{1}{2}$ a per cent. at most) the ratio of ionizations should be proportional to unity—that is, the ratio should be constant. Within the limit of experimental error, that is to about 2 per cent., the ratio was found to be constant. We may therefore conclude that the quality and intensity of the radiation scattered at right angles to the incident radiation by filter-paper is, under the conditions of experiment described above, to a close approximation in agreement with the theory of Compton, and not with the classical theory. But the "scattered" absorption under the same conditions of experiment was also found to be in agreement with the former theory, so that it seems very probable that the excess corpuscular radiation of paper and aluminium, observed in the previous experiment, arises from the process of scattering.

Attention should perhaps be called to the apparently discontinuous nature of the curves in Graphs IV. and V. The observations appear to lie on two or perhaps three curves lying in echelon. Where the curves overlap we get two values of the ordinate for one of the abscissa, or *vice versa*. The small circles in Graph V. (which represent single observations, and not averages of observations) are seen to lie very close to one or other of the curves drawn—so close, in fact, that in practically every case there is no doubt as to which curve each circle belongs to. As no observations have been suppressed, it would seem that the discontinuities are real, and not due to experimental error. The higher values of μ/ρ Secondary, where there are two for the same value of μ/ρ Primary, are much less numerous than the lower, so we may consider the higher value the exceptional case. The lower values are of the order calculated on Compton's theory. It should be pointed out that the higher values were not obtained consecutively. Table VII. gives the observations in the order in which they were taken, and those which definitely gave the higher or exceptional values, six in number, are marked with a star. It will be noticed that the higher values are distributed fairly uniformly throughout the series, and cannot therefore be attributed to any temporary fault in the apparatus. The probability that the effect is genuine is strengthened by the fact that other observers in this laboratory have found similar discontinuities at the same wave-lengths in performing the experiment under different conditions. While the effect may be due to the heterogeneity of the radiation, for only very thin filters were used, the possibility of a more fundamental origin should not be overlooked. When the radiation is very hard, the scattered radiation is directed strongly in the forwards direction, according to Compton's theory, and the relative intensity of the radiation at 90° is reduced. The presence of the tungsten K-lines in the incident radiation would for this reason produce less than its due effect in the secondary, and the average penetrating power of the secondary would on this account alone be less than that of the primary. This effect, combined with the normal softening of the radiation, would give too high a value of μ/ρ, Secondary, on our curve. The results obtained with very heterogeneous beams, where the exact nature of the heterogeneity is not known, would therefore appear to be difficult to interpret.

General Discussion of Results of Experiments.

The results of the experiments which have just been described have been shown to be in general agreement with the description of the process of scattering due to Compton. It seems impossible, however, to reconcile the results of Compton with those of Clark and Duane without assuming the existence of alternative processes of scattering. The absence of discontinuities in the absorption curves given in Graph I., when compared with the marked discontinuities in the curves of Barkla and White, would appear to require the assumption of the existence of alternative processes of absorption. It seems probable that these two phenomena are not unconnected with one another. I understand that Professor Barkla is about to publish some experimental results which may throw some light on this subject.

Summary.

Experiments on the relative absorptions of X-rays by copper, aluminium, and paper, under conditions detailed, show that under these conditions the J-discontinuities of Barkla and White do not appear. The results indicate that the absorption associated with scattering falls below the classical value by an amount which agrees very well with that calculated on the quantum theory of scattering of A. H. Compton.

Experiments on the ionization of sulphur dioxide and ethyl bromide give no certain indication of the existence of J-discontinuities, but they give some evidence for the existence of an abnormal corpuscular emission from air such as would be accounted for by the Compton theory.

Experiments on the corpuscular emission from paper, aluminium, copper, and lead, as measured by ionization of hydrogen, showed that the lighter elements emitted an additional corpuscular radiation when the wave-length of the incident radiation was short, that the energy required for the excess emission produced no apparent discontinuity in the absorption curve for paper, but they lent support to the view of Compton that a corpuscular emission would be found in association with scattering when the primary was of short wave-length.

An experiment on the scattering of X-rays by filter-paper showed that the change in quality and the variation in intensity of the scattered radiation required by Compton's theory were confirmed over a considerable range of wave-lengths for scattering at right angles to the primary. From this it was deduced that the scattered X-rays were probably carrying only a fraction of the energy absorbed in association with scattering, thus strengthening the probability that the excess corpuscular emission observed in the previous experiments was to be attributed to the scattering process.

The experiments were carried out under the direction and supervision of Professor Barkla, and I take this opportunity of thanking him and expressing my appreciation of the generous amount of assistance he has given during the conduct of the experiments and in preparing the results for publication.

XXIV. *The Production of Sub-Harmonics. By* W. N. Bond, *B.A., D.Sc., F.Inst.P.* (*Lecturer in Physics, University College, Reading*) [*].

[Plate IV.]

THIS paper consists of a detailed consideration of the sub-harmonic notes, produced by the intermittent contact of a tuning-fork and a suitable solid body, that have been previously described and demonstrated [†]. The experimental conditions will be described briefly before discussing the mechanism of the phenomenon.

When a large unmounted tuning-fork is energetically sounded, and part of the stem or the basal end of its prongs is touched lightly against a fixed solid body, some note may be produced that has a frequency equal to that of the fork divided by a small integer. As many as five different notes may thus be obtained, the smaller frequencies being produced when the amplitude of the fork is large or the force pressing the fork against the body small. The intermittent nature of the contact may be demonstrated by using a metal block for the fixed body, and completing a circuit containing an ammeter or a telephone in series with the contact and a cell. The ammeter gives different mean currents for the different sub-harmonics, and the telephone emits the corresponding notes. By using a Deprez electromagnetic signal-marker in the circuit, graphical records of the current have been obtained, and the frequencies are found to be all sub-multiples of that of the fork. This is illustrated in Pl. IV. fig. 1, where the intermittent current has frequencies equal to that of the fork (288) and its first four sub-harmonics. An intermittent current of frequency 50, also shown, was used as a standard for measurement. Experimental values of the frequencies, thus obtained, are given in the Plate.

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[*] Communicated by the Author.

[†] 'Nature,' March 8th, 1924, and Proc. Phys. Soc., August 1924.

The shape and material of the fixed body may be varied considerably, and yet the notes are obtained. But the notes are most clearly emitted when a hard metal body of high natural frequency and high elastic constants is employed (provided the metal be not such as to emit a jangle when contact is made).

Since the use of a fixed body of low natural frequency does not make the notes less difficult to obtain, it may be concluded that the intermittent nature of the contact is due to the rebound of the fork from the body (and not to a momentary depression in the surface of the body), a whole number of periods of the fork elapsing between successive contacts.

The graphical records consist of three types. Firstly, quite irregular records are found. The coarse note that these correspond to may be avoided by letting the fork approach the block very gradually. Secondly, regular records occur, such as are shown in Pl. IV. fig. 1. And thirdly, in some records the intervals between successive contacts vary, but each interval appears on casual inspection to correspond to one of the sub-harmonics (fig. 2).

If the production of the notes be supposed to be due to contact of the fork and body, a rebound of the fork, and its subsequent return because of the small applied force, various peculiarities require explanation. When the fork amplitude is large and the applied force and original velocity are small, the notes are almost invariably produced, without special adjustment of the conditions. The value of the applied force may fluctuate, and the amplitude of the fork decrease gradually, and yet as many as a hundred equal consecutive waves may occur in the case of the higher frequency notes. (Only sets of about ten consecutive waves were obtained for the fourth sub-harmonic.) And, finally, the successive intervals may differ, each being, however, approximately equal to a simple multiple of the period of the fork.

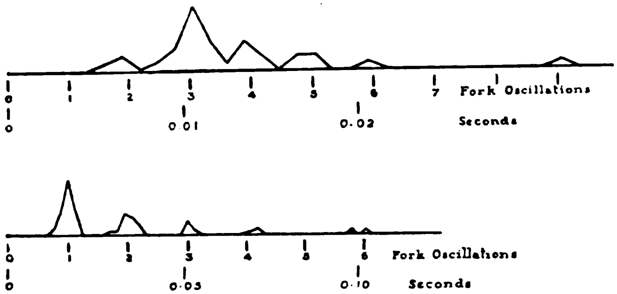
The only theory that seems to satisfy all these conditions is that the velocity of approach of the fork and block, just before an impact occurs, is small compared with the average velocity of oscillation of the part of the fork considered (measured in the direction of the normal to the surface of contact). If this condition were satisfied at each impact, contact would invariably occur when the part of the fork was near the outward end of its oscillation; and hence any interval between impacts would only differ from a multiple of the fork's period by a small fraction of this period. It has been shown that the relative velocity of fork and body should be small at the commencement of the experiment; but for it also to be small at the end of *each* interval it must be small just after each impact, unless the motion of the fork as a whole be supposed damped. (And damping cannot in general be supposed important, as the higher notes may be obtained when the fork is erect and rests almost unheld, with its stem on the solid body.)

The relative velocity of the two surfaces just before contact is equal to the small velocity of approach, together with the larger velocity of oscillation of the portion of the fork making contact. That the consequent velocity of departure is small may be considered due to the contact being of the nature of an impulse. The surfaces in contact must be supposed appreciably deformed during a typical impact. The magnitude of the impulse will depend chiefly on the amplitude of the fork and the phase when contact commences; and the velocity of departure of the fork will depend also on the mass of the fork (or its moment of inertia, if it be supported by a pivot).

In order to test this hypothesis, it was decided to measure the intervals in a record of a series of impacts, where the successive intervals corresponded to various sub-harmonics. A graph obtained with the fork of frequency 288 was first used; and the positions at which contact occurred were compared with an ideal series such as would have occurred if contact had been made at the same phase at each oscillation of the fork. Owing to the necessity of any error of recording and measurement being considerably less than 1/288 of a second, the experiment was repeated using a fork of frequency 59·1 ± 0·04. With such a low note the sub-harmonics could not be heard, though they appear on the records (Pl. IV. fig. 2).

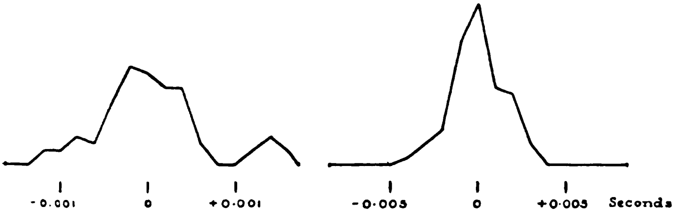
Observed intervals between consecutive impacts are represented statistically in fig. 3 from experiments with the 288 and 59·1 forks. It will be noticed that the intervals are approximately whole multiples of the period of the fork, but that deviations occur. In the case of the 288 fork, a few observed intervals differ by almost half a fork-period from being an integral number of fork oscillations. No such large deviations were found with the slower fork, and they may therefore be supposed to be due to experimental errors.

Fig. 3.



In fig. 4 the difference, (observed time of contact — time of ideal contact) is plotted statistically for the two forks. The ideal series was chosen so that the algebraic mean of the above differences was zero for any particular series of impacts. The figure shows that, on the average, the times of contact differ from the ideal times by about a sixth of a period of the fork.

Fig. 4.



When a time of contact differs from that of the ideal set, it is found that in about 80 per cent. of the cases the next impact differs by a smaller amount or by an amount of the reverse sign (see Pl. IV. fig. 2). And when a record is almost entirely that of a single sub-harmonic (Pl. IV. fig. 1), the deviations plotted in fig. 4 become appreciably less. At the commencement of regular intermittent motion it was found that the successive periods approach more and more closely to the ideal period. These facts are explained by the theory put forward. For, a contact that is markedly earlier in phase than the extremity of the fork's oscillation will produce an abnormally large velocity of rebound ; and the succeeding contact will occur when the fork's phase is abnormally late.

The following interval will in consequence, be specially short.

No particular conditions have been noticed always to precede an interval a number of periods longer in duration than the former one (when intervals corresponding to various sub-harmonics are occurring in rapid succession). This fluctuation between various sub-harmonics may be due to change in the applied force or to slight shifting of the point of contact.

Apart from any bearing of the experiments on theories of hearing, one simple practical application may be mentioned. Provided a suitable recording arrangement is available, the frequency of any unmounted fork can be obtained by attaching a fine wire to its stem, bowing the fork, and making intermittent contact between the fork's stem and a metal block (as described above). The frequency of a simple fork, unmodified by any stile, is thus obtained, without the need of an elaborate microphonic or stroboscopic device.

In conclusion, the Author would like to thank Prof. J. A. Crowther and Mr. A. W. P. Wolters for the facilities that have made these experiments possible; and Mr. J. L. Dunk for interesting points that have arisen during correspondence on the subject.

XXV. *Fluid Circulation Round Cylindrical Obstacles.* *By* D. M. WRINCH, *D.Sc., Lecturer at Lady Margaret Hall, Oxford* *.

SUMMARY.

THIS paper treats of the motion of a fluid circulating round a fixed cylindrical obstacle in the presence of one or more line sources or sinks in any case when *c* the curve of cross-section of the obstacle has an equation of the form

$$x=a\cos u+a_1\cos(\alpha_1-u)+a_2\cos(\alpha_2-2u)+\ldots,$$
$$y=a\sin u+a_1\sin(\alpha_1-u)+a_2\sin(\alpha_2-2u)+\ldots,$$

the parameters (a_n, α_n) being suitably restricted.

The problem of a fluid circulating round a cylindrical obstacle in the presence of a single sink is discussed in detail. The resultant pressure on the obstacle is easily found by the evaluation of the contour integral

$$\int_c (dW/dz)^2 dz,$$

where

$$W=\phi+i\psi,$$

and ϕ is the velocity potential and ψ the stream-function associated with the motion.

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* Communicated by the Author.

The problem when there is a source as well as a sink is also discussed. This problem, when the positions of the source and sink are suitably chosen, easily gives, as a degenerate case, the problem of fluid streaming past and circulating round a cylindrical obstacle. A similar contour integration along c, the curve of cross-section of the obstacle, yields the result that the force on the obstacle per unit length is $\rho k q$ in a direction $\pi/2$ from the direction of the undisturbed stream measured in the sense opposite to the sense of the circulation, where ρ is the density of the fluid, k the intensity of circulation, and q the velocity in the undisturbed stream.

THIS paper treats the motion of a fluid outside a fixed cylindrical obstacle in the presence of one or more line sinks or sources when there is circulation round the obstacle.

A frontal attack is made on the problem on this occasion by the discussion of the whole range of cases when the cross-section of the obstacle has an equation of the form

$$x = a\cos u + a_1 \cos(\alpha_1 - u) + a_2 \cos(\alpha_2 - 2u) + \ldots,$$

$$y = a\sin u + a_1 \sin(\alpha_1 - u) + a_2 \sin(\alpha_2 - 2u) + \ldots,$$

certain restrictions being made as to the values which may be assumed by the various parameters (a_n, α_n). Any number of the parameters a_n may vanish, and this specification evidently covers the cases generally discussed, such as, for example, the circle, the ellipse, and the hypotrochoid.

The restrictions on the parameters (a_n, α_n) do not allow the inclusion of cases when the curve of cross-section of the obstacle has a node. It is possible, however, to include cases when the curve has a cusp, but in all such cases when there is a single source or sink outside the obstacle an infinite velocity is in general associated with the cusp, and the motion in each case cannot be realized with a finite pressure in the fluid. This is also the case when there is circulation about the obstacle. But if there is circulation k round the obstacle in the presence of a single sink or source of strength m, it is possible to choose the ratio of k to m in such a way that the velocity at the cusp remains finite. The resulting motion is then possible with a finite pressure at infinity, provided that this pressure is sufficiently large.

In this paper the various problems are attacked in general for any value of the circulation and for sources and sinks of any strengths so long as the curve of cross-section of the obstacle has no cusps. If the curve of cross-section has a cusp, the problem is discussed only when the magnitude of the circulation is such as to produce with the sources and sinks a finite velocity at the cusp.

The solution of the problem when there is circulation about an obstacle and a single sink is given in detail, and by an application of the theory of contour integration the resultant pressure on the obstacle per unit length is easily found. The problem when there is a line source and a line sink in addition to circulation round the obstacle is also mentioned. Finally, the problem of streaming past the obstacle round which there is circulation, which is a degenerate case of the preceding problem when the positions of the source and sink are suitably chosen, is discussed. The resultant pressure on the obstacle in this case is proved to be the product of the density of the fluid and the circulation and the velocity of the stream at infinity, and to act in a direction $\frac{\pi}{2}$ from the direction of the stream at infinity measured in the sense opposite to that of circulation. This result, known as the Kutta-Joukowski Lift Formula, is proved by Joukowski [*] by general dynamical principles. The alternative proof given in the present paper proceeds by means of a simple application of the theory of contour integration which allows the rapid calculation of the resultant pressure on an obstacle due to any motion. It is deemed worthy of inclusion in this paper because of the great importance of the Lift Formula in the Circulation Theory of Lift [†] now under discussion in Aerodynamics.

I. *A line sink in the presence of a cylindrical obstacle.*

Suppose that there is a line sink of strength m at a point z_0 outside a cylinder. The line sink alone in space has the W-function W_0 given by

$$W_0=\phi_0+i\psi_0=\frac{m}{2\pi}\log(z_0-z),$$

where ϕ_0 is the velocity potential and ψ_0 the stream-function associated with the motion. Let W_1 represent the disturbance due to the presence of the cylinder, so that the motion when the sink is in the presence of the cylinder is given by

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[*] N. Joukowski, *Aérodynamique* (*traduit du russe par* S. Drzewiecki), Paris, 1916, chap. vi.

[†] See F. W. Lanchester, 'Aerodynamics,' ch. iv.; A. R. Low, 'The Circulation Theory of Lift,' International Air Congress, London, 1923; 'Dictionary of Applied Physics,' vol. v. 1923; 'The Hydrodynamical Theory of Wing-surfaces,' pp. 217–220; and other text-books.

$$W=\phi+i\psi=W_0+W_1=\phi_0+\phi_1+i(\psi_0+\psi_1).$$

Then we require that W_1 shall be evanescent on the circle at infinity, and that it shall satisfy Laplace's equation and have no singularities between the circle at infinity and c the curve of cross-section of the cylinder, and further that ψ shall be constant on c.

Now consider the transformation

$$z=ae^{iw}+a_1e^{i\alpha_1-iw}+a_2e^{i\alpha_2-2iw}+\ldots, \quad . \quad . \quad . \quad . \qquad (1\cdot1)$$

where

$$w=u+iv,$$

which has the property that $v=-\infty$ on the circle at infinity. Then $v=0$ on the curve whose equation is given by

$$z=ae^{iu}+a_1e^{i\alpha_1-iu}+a_2e^{i\alpha_2-2iu}+\ldots,$$

or

$$\left.\begin{aligned} x&=a\cos u+a_1\cos(\alpha_1-u)+a_2\cos(\alpha_2-2u)+\ldots,\\ y&=a\sin u+a_1\sin(\alpha_1-u)+a_2\sin(\alpha_2-2u)+\ldots. \end{aligned}\right\} \quad (1\cdot2)$$

Suppose, further, that the constants in the transformation (1) are such that for values of v between zero and $-\infty$, dz/dw has no zeros and no infinities. Then we may at once solve the problem of the sink outside a cylindrical obstacle in all cases where, for some value or other of the various constants satisfying the condition with respect to the zeros and infinities of dz/dw, the equation of c, the curve of cross-section of the cylinder, is given by (1·2).

For, in terms of the complex variable w, we have

$$\begin{aligned} W_0=\frac{m}{2\pi}\log\{&ae^{iw_0}+a_1e^{i\alpha_1-iw_0}+a_2e^{i\alpha_2-2iw_0}+\ldots\\ &-(ae^{iw}+a_1e^{i\alpha_1-iw}+a_2e^{i\alpha_2-2iw}+\ldots)\}\\ =\frac{m}{2\pi}\log(&e^{iw_0}-e^{iw})\{a-a_1e^{i\alpha_1-iw_0-iw}\\ &-a_2e^{i\alpha_2}(e^{-iw-2iw_0}-e^{-iw_0-2iw})-\ldots\}, \end{aligned}$$

w_0 being given by

$$z_0=ae^{iw_0}+a_1e^{i\alpha_1-iw_0}+a_2e^{i\alpha_2-2iw_0}+\ldots.$$

Since z_0 lies in the region between c and the circle at infinity, v_0 lies between zero and $-\infty$. We may evidently expand W_0 in a series convergent in the neighbourhood of the curve c in the form

$$W_0 = \frac{miw_0}{2\pi} - \frac{m}{2\pi}\left(e^{iw-iw_0} + \tfrac{1}{2}e^{2iw-2iw_0} + \dots\right)$$
$$+ \frac{m}{2\pi}\log\left(a - a_1 e^{-iw_0-iw}\dots\right).$$

Then, if we write

$$W_1 = -\frac{m}{2\pi}\left(e^{v_0}e^{-iw+iu_0} + \tfrac{1}{2}e^{2v_0}e^{-2iw+2iu_0} + \dots\right)$$
$$-\frac{m}{2\pi}\left\{\log\left(a - a_1 e^{-iw_0-iw}\dots\right) - \log a\right\},$$

W_1 is evanescent on the circle at infinity and, further

$$W = \frac{miw_0}{2\pi} - \frac{m}{\pi}\left\{e^{v_0}\cos(w-u_0) + \tfrac{1}{2}e^{2v_0}\cos 2(w-u_0) + \dots\right\}.$$

With this determination of W we have

$$\phi = -\frac{mv_0}{2\pi} - \frac{m}{\pi}\left\{e^{v_0}\cos(u-u_0)\cosh v\right.$$
$$\left. + \tfrac{1}{2}e^{2v_0}\cos 2(u-u_0)\cosh 2v + \dots\right\},$$

$$\psi = \frac{mu_0}{2\pi} + \frac{m}{\pi}\left\{e^{v_0}\sin(u-u_0)\sinh v\right.$$
$$\left. + \tfrac{1}{2}e^{2v_0}\sin 2(u-u_0)\sinh 2v + \dots\right\},$$

and on the curve c, ψ is constant and equal to $\frac{mu_0}{2\pi}$. We therefore have the W-function for the motion when the sink m at z_0 is in the presence of the cylindrical obstacle whose cross-section is the curve c given by (2).

II. *Circulation about a cylinder in the presence of a line sink.*

We may also solve the more general problem of a circulation $-k$ about this cylinder in the direction u increasing when there is a line sink m at the point z_0. We evidently have

$$W = \frac{kw}{2\pi} + \frac{miw_0}{2\pi} - \frac{m}{\pi}\left\{e^{v_0}\cos(w-u_0) + \tfrac{1}{2}e^{2v_0}\cos 2(w-u_0)\dots\right\}.$$

III. *The pressure on the cylinder.*

It is a simple matter to find the resultant pressure on the obstacle in the presence of the sink, and also in the more general case when there is circulation round the obstacle in addition. For let q represent the velocity at any point and ϕ the angle which the velocity makes with the axis of x in the case of the sink m and circulation $-k$. Then

$$qe^{-i\phi}=d\mathrm{W}/dz=\frac{k}{2\pi}+\frac{m}{\pi}\{e^{v_0}\sin(w-u_0)+e^{2v_0}\sin 2(w-u_0)+\ldots\}$$

$$=k/2\pi+\frac{m}{2\pi}\frac{e^{v_0}\sin(w-u_0)}{\cosh v_0-\cos(w-u_0)}.$$

The pressure at any point is given by

$$p=-\tfrac{1}{2}\rho q^2+\text{constant}.$$

We will discuss only those motions in which q is finite everywhere except at the sink, for these motions alone are physically possible. Now $d\mathrm{W}/dw$ is infinite only at the sink. Further, dz/dw is never zero between the curve c and the circle at infinity. On the curve c, however, we can admit a simple zero of dz/dw and consequently a cusp, provided that the ratio of k/m is so chosen that $d\mathrm{W}/dw$ has a zero at this point. Thus suppose that dz/dw has a simple zero at the point $u=v=0$ on the curve c. If we choose the ratio k/m in such a way that $d\mathrm{W}/dz$ vanishes at this point, so that, in fact,

$$me^{v_0}\sin u_0=k(\cosh v_0-\cos u_0), \quad . \quad . \quad . \quad (3.1)$$

the velocity is still everywhere finite. We therefore deal with the general case of a sink m and circulation $-k$ when the curve c has no cusps and with the case when the curve has a cusp or cusps only when the ratio k/m can be and is so adjusted as to make the velocity at the cusp or cusps remain finite.

Let p_x and p_y be the resultant pressures in the directions x and y. Then

$$p_y+ip_x=\int p(dx-idy)$$

$$=-\tfrac{1}{2}\rho\int q^2(dx-idy),$$

the integrations being taken along the curve. But on the curve c the velocity is wholly tangential to the curve.

Therefore on c

$$q^2(dx-i\,dy)=(dW/dz)^2(dx/ds+i\,dy/ds)^2(dx-i\,dy)$$
$$=(dW/dz)^2(dx+i\,dy).$$

Thus

$$p_y+ip_x=\tfrac{1}{2}\rho\int_c q^2(dx-i\,dy)=\tfrac{1}{2}\rho\int_c (dW/dz)^2 dz\,\text{*}.$$

To integrate $(dW/dz)^2$ round the curve c in the z-plane, we use the transformation

$$z=ae^{iw}+a_1e^{i\alpha_1-iw}+a_2e^{i\alpha_2-2iw}+\ldots,$$

and write

$$t=e^{-iw}.$$

Then the integration of $(dW/dz)^2$ round the curve c becomes the integration round the unit circle $t=e^{i\theta}$ in the t-plane from $\theta=\pi$ to $\theta=-\pi$ of

$$(dW/dz)^2 dz/dw\,.\,dw/dt=(dW/dw)^2.\,(dw/dt)/(dz/dw).$$

Now

$$dW/dw=\frac{m}{2\pi}\cdot\frac{\sin(w-u_0)}{\cosh v_0-\cos(w-u_0)}+\frac{k}{2\pi}$$
$$=-\frac{mi}{2\pi}\,\frac{t^2e^{v_0}-t_0{}^2e^{-v_0}}{(t-t_0)(te^{v_0}-t_0e^{-v_0}}+\frac{k}{2\pi},$$

and

$$(dw/dt)/(dz/dw)=1/(a-a_1t^2e^{i\alpha_1}-2a_2t^3e^{i\alpha_2}\ldots.).$$

There is evidently no pole of the integrand at $t=0$ and only a pole therefore at $t=t_0=e^{-iw_0}$. There is no pole on the contour of integration corresponding to a point on the curve c, for in the cases when there is a zero of dz/dw at such a point the ratio of k/m is so chosen as to produce a zero in dW/dw at the same point.

Now putting $t=t_0+\epsilon$, we have

$$(dW/dw)^2(dw/dt)/(dz/dw)$$
$$=\left[\frac{k}{2\pi}-\frac{mit_0}{\pi e}\cdot\frac{t_0\sinh r_0+\epsilon e^{v_0}\ldots}{2t_0\sinh r_0+\epsilon e^{v_0}\ldots}\right]^2\Big/aA(1-\lambda\epsilon\ldots)$$
$$=\frac{1}{aA\epsilon^2}\left\{\frac{k\epsilon}{2\pi}-\frac{mit_0}{2\pi}\left(1+\frac{\epsilon e^{v_0}}{2t_0\sinh v_0}\right)\right\}^2(1+\lambda\epsilon)+\ldots,$$

provided that

$$a-a_1t^2e^{i\alpha_1}-2a_2t^3e^{i\alpha_2}\ldots=aA(1-\lambda\epsilon+\ldots).$$

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* This theorem is sometimes referred to as Blasius's Theorem.

Thus the residue at t_0 is given by

$$\frac{1}{Aa}\left\{\left(\frac{mit_0}{2\pi}\right)^2\lambda-\frac{mit_0}{\pi}\left(\frac{k}{2\pi}-\frac{mie^{v_0}}{4\pi\sinh v_0}\right)\right\}.$$

The value of the integral is therefore

$$\frac{2\pi i}{aA}\cdot\frac{mt_0}{2\pi}\left\{\frac{mt_0\lambda}{2\pi}+\frac{ik}{\pi}+\frac{me^{v_0}}{2\pi\sinh v_0}\right\}$$

$$=\frac{mie^{-iu_0}}{2\pi aA}\left\{\frac{me^{v_0}}{\sinh v_0}+me^{-iu_0}\lambda+2ik\right\},$$

the integration along the unit circle $|t|=1$ being taken in the clockwise direction. Therefore we have

$$-p_y-ip_x=\tfrac{1}{2}\rho\int_c(dW/dz)^2dz$$

$$=\frac{m\rho}{4\pi aA}\left\{\frac{me^{v_0}}{\sinh v_0}u^{-iu_0}-2ke^{-iu_0}+m\lambda ie^{-2iu_0}\right\}.$$

It is of particular interest to notice the presence of the force due to the combination of circulation with the sink. This "lift" acts in a direction determined by the orientation of the sink with respect to the obstacle and by the argument of A, which also depends on this orientation and on the equation of c, the curve of cross-section. It is also of interest to notice the critical value, given in (3.1), of the ratio k/m requisite in the case of a cusped curve if an infinite velocity at the cusp is to be avoided.

The case when the curve c is symmetric about the axis of x is of special interest. We then have $\alpha_1=\alpha_2\ldots=0$, and a simpler form results. If, in addition, we are concerned only with a sink on this axis of symmetry on the positive side $u_0=0$, and with A and λ wholly real, we have

$$p_y=m\rho ke^{v_0}/2\pi aA,$$

$$p_x=-\frac{m^2\rho e^{2v_0}}{4\pi aA}\left(\frac{1}{\sinh v_0}+\lambda\right).$$

Thus the sink m exerts a force proportional to the product mk in a direction $\pi/2$ from the direction of the x-axis measured in the sense opposite to that of the circulation k. It also exerts a force proportional to m and independent of k along the x-axis. It therefore appears that the lift in this case is perpendicular to the line joining the sink to the origin of coordinates.

IV. *The pressure on a circular cylinder.*

Thus, to take a simple example of this result: if c is a circle of radius a, $A=1$, $\lambda=0$, and a sink at a point f from the centre on the positive side of the x-axis together with circulation k clockwise yields the forces

$$p_y = m\rho k/4\pi f,$$
$$p_x = m^2\rho a^2/2\pi f(f^2 - a^2).$$

Thus the sink attracts the cylinder with a force

$$m^2\rho a/2\pi f(f^2 - a^2)$$

per unit length along the line joining the centre to the sink, and provides also a transverse lifting force

$$m\rho k/4\pi f$$

per unit length in a direction $\pi/2$ from this line in the counter-clockwise direction. And it is to be remarked that a source m would in the same way attract the cylinder along the line joining it to the centre of the cross-section; the transverse force in this case would, however, be in a direction making an angle $\pi/2$ measured clockwise with this line.

V. *The pressure on an elliptic cylinder.*

As another simple illustration we may consider the forces when a line sink m is situated at a point f on the x-axis outside the elliptic cylinder

$$x = \alpha \cos u,$$
$$y = \beta \sin u.$$

Here we have the transformation

$$z = ae^{i\kappa} + a_1 e^{-i\kappa}$$

with

$$a = \tfrac{1}{2}(\alpha + \beta), \qquad b = \tfrac{1}{2}(\alpha - b).$$

Further, $u_0 = 0$ and

$$f = ae^{-v_0} + a_1 e^{v_0},$$

so that

$$e^{v_0} = (f - \sqrt{f^2 - 4aa_1})/2a_1 = (f - \sqrt{f^2 - c^2})/(\alpha - \beta),$$

where

$$e^2 = \alpha^2 - \beta^2$$

and

$$e^{-v_0} = (f + \sqrt{f^2 - 4aa_1})/2a = (f + \sqrt{f^2 - c^2})/(\alpha + \beta),$$

so that

$$\sinh v_0 = (f - \sqrt{f^2 - c^2})/2(\alpha - \beta) - (f + \sqrt{f^2 - c^2})/2(\alpha + \beta)$$
$$= (f\beta - \alpha\sqrt{f^2 - c^2})/c^2.$$

Also
$$dz/dw=\frac{ai}{t}\left(1-\frac{a_1}{a}t^2\right).$$

Therefore
$$aA=a\left(1-\frac{a_1}{a}t_0{}^2\right)$$
$$=a\left(1-\frac{a_1}{a}e^{2v_0}\right)$$
$$=e^{v_0}\sqrt{f^2-c^2},$$

and
$$aA\lambda-2a_1t_0=(\alpha-\beta)e^{v_0}.$$

Thus
$$p_y=kme/4\pi(f^2-c^2)^{1/2},$$

$$p_x=\frac{m^2\rho e^{v_0}}{4\pi(f^2-c^2)^{1/2}}\left\{\frac{\alpha^2-\beta^2}{\alpha(f^2-c^2)^{1/2}-\beta f}-\frac{\alpha-\beta}{(f^2-c^2)^{1/2}}\right\}$$
$$=\frac{m^2\rho[f-(f^2-c^2)^{1/2}]\beta[f+(f^2-c^2)^{1/2}]}{4\pi[\alpha(f^2-c^2)^{1/2}-pf](f^2-c^2)}$$
$$=\frac{m^2\rho\beta c^2}{4\pi(f^2-c^2)\{\alpha(f^2-c^2)^{1/2}-\beta f\}}.$$

VI. *Circulation about a cylinder in the presence of a number of line sources and sinks.*

We may, after the same manner, find the motion when there is circulation round the cylinder and any number of line sinks or sources outside. Thus, if there is a source m at a point z_0' in addition to a sink m at a point z_0 where

$$z_0=ae^{iw_0}+a_1e^{i\alpha_1-iw_0}+a_2e^{i\alpha_2-2iw_0}\ldots.$$
$$z_0'=ae^{iw_0'}+a_1e^{i\alpha_1-iw_0'}+a_2e^{i\alpha_2-2iw_0'},$$

the motion is given by

$$W=\frac{kw}{2\pi}+\frac{mi}{2\pi}(w_0-w_0')-\frac{m}{\pi}\{e^{v_0}\cos(w-u_0)$$
$$-e^{v_0'}\cos(w-u_0')+\ldots.\}.$$

In particular, if $w_0'=w_0+\pi$, so that

$$v_0'=v_0,\qquad u_0'=u_0+\pi,$$

and

$$W=\frac{kw}{2\pi}+\frac{mi}{2}-\frac{2m}{\pi}\{e^{v_0}\cos(w-u_0)$$
$$+\tfrac{1}{3}e^{3v_0}\cos(w-u_0)+\ \ldots\}.$$

If, now, we make $m \longrightarrow \infty$ and $|z_0| \longrightarrow \infty$ in such a way that

$$m/\pi z_0 = q_0,$$

we get streaming past the cylinder, the velocity of the stream before it is disturbed by the presence of the cylinder being q_0 in a direction making an angle u_0 with the axis of x, and

$$W = \frac{kw}{2\pi} - 2aq_0 \cos(w - u_0)$$

and

$$\frac{dW}{dw} = \frac{k}{2\pi} + 2aq_0 \sin(w - u_0).$$

Thus, in the case of a curve of cross-section for which $dz/du = 0$ at $u = u_1$, we need to take

$$k = 4\pi aq_0 \sin(u_0 - u_1)$$

if an infinite velocity at the cusp is to be avoided.

The value of p_x and p_y can be found at once. We have

$$\int_c (dW/dz)^2 dz$$

$$= \int_{c'} \left\{ \left[\frac{k}{2\pi} + iaq_0\left(te^{iu_0} - \frac{1}{t}e^{-iu_0}\right)\right]^2 \Big/ \left[a - a_1 t^2 e^{i\alpha_1} \ldots.\right] \right\} dt,$$

the latter integration being taken round c' the unit circle $|t| = 1$ in a clockwise direction. The only pole is the double pole at the origin: there is, as before, no pole on the contour of integration even if dz/dw has a zero at such a point, for under those circumstances the ratio k/q_0 is so chosen as to produce a zero in dW/dw at that point. Thus

$$\int_c (dW/dz)^2 dz = -2q_0 k e^{-iu_0},$$

and

$$p_x = -\rho q_0 k \sin u_0,$$

$$p_y = \rho q_0 h \cos u_0.$$

Thus the resultant force is $\rho q_0 k$ in a direction making $\pi/2$ with the direction of the undisturbed stream measured in the sense opposite to that of circulation. This is the Kutta-Joukowski result *, which is of importance in Aerodynamics.

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* See Joukowski, *loc. cit.*; also Lamb, 'Hydrodynamics,' 5th edition, pp. 76, 647.

XXVI. *The J Transformation of Scattered X-Rays.* *By* C. G. Barkla, *F.R.S.*, *and* S. R. Khastgir, *Ph.D.*, *University of Edinburgh* *.

Since the earliest experiments on the scattering of X-rays it has been known that certain condtions were necessary in order to obtain *evidence* of the purest scattering of X-radiation. Under these conditions, through a wide range of wave-lengths, the secondary radiation did not differ appreciably in penetrating power from the primary. It was *this* secondary radiation, and no other, which was called the scattered X-radiation ; it was this which we showed could be explained in its polarization, in its distribution, in its intensity, precisely by the application of the classical theory as given by J. J. Thomson. (It gave exactly the number of extra-nuclear electrons per atom.) In the experimental investigations it was observed or arranged that the complications appearing under other conditions were not introduced.

Under other conditions—conditions which appear to have been obtained by many experimenters on the subject—there was a marked difference between the primary and secondary radiation *as observed.* (See Phil. Mag. April 1923 : Barkla and Mrs. Sale.) Whatever the explanation—there were several possibilities—this secondary radiation was obviously something different from the scattered radiation. This, however, has *also* recently been called by Compton the scattered radiation, and the classical theory of scattering has then been described as inadequate. As the classical theory of scattering was intended only to explain scattering, it is not surprising that it does not cover the other phenomenon which has been given the same name.

This phenomenon has been briefly discussed by one of us in a letter to 'Nature' †, and more fully in a lecture to the Röntgen Society ‡, and its application to the scattering of X-rays has been indicated. A fuller treatment of the subject will appear in other papers, but we propose to give a short description of one only of a series of experiments showing how the true nature of the phenomenon of scattering has in many cases been obscured.

Preliminary results of the kind described in this paper were obtained by Barkla and Mrs. Sale several years ago (1921–22); but they were so new, so puzzling, that they were withheld from publication for more careful and critical examination. The results were these:—When primary and secondary rays were compared by their power of penetrating thin absorbing sheets, they appeared practically identical; but thicker absorbing sheets showed a most decided difference (about 12 per cent. in absorption coefficient).

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* Communicated by the Authors.

† November 17, 1923.

‡ A summary only has been published in 'Nature,' November 22, 1924. A more detailed account will be given in the Journal of the Röntgen Society.

Again, it was found necessary to use thin radiators to obtain scattered rays like the primary throughout a long range of wave-lengths. This is indicated on p. 747 *. "When thin sheets of paper were used as the scattering substance—in which case trouble due to differential absorption of primary and secondary beams in the radiating substance was avoided—experiments showed that the scattered was identical with the primary radiation throughout almost the whole range of wave-lengths experimented upon." The complication evidently introduced by thick radiating sheets was purposely avoided in order to obtain the conditions most favourable to the study of fundamental processes.

The experiment described below showed, as in many previous experiments, that the secondary radiation from paper was originally exactly like the primary radiation in penetrating power. When secondary and primary radiations were transmitted through equal thin sheets of aluminium, this equality of penetrating powers persisted only up to a certain critical thickness of absorbing material. An abrupt absorption of the secondary radiation then occurred, and the transmitted radiation was subsequently more absorbable than the primary radiation which was transmitted through exactly the same thickness of aluminium.

Thus the scattered X-radiation was modified by the J phenomenon quite outside the scattering substance, and afterwards appeared as what A. H. Compton regards (presumably) as the quantum scattered radiation. As we have said previously, the phenomenon here has no connexion with the *process* of scattering. Its association with the scattered radiation is quite accidental,—in the sense that it is not fundamental,—for an exactly similar phenomenon may be shown with a primary radiation.

Experiment.

The experiment was quite a simple one. A and B were two ionization chambers—one, A, receiving pencils of primary radiation ; B receiving radiation scattered from the paper sheets R (fig. 1).

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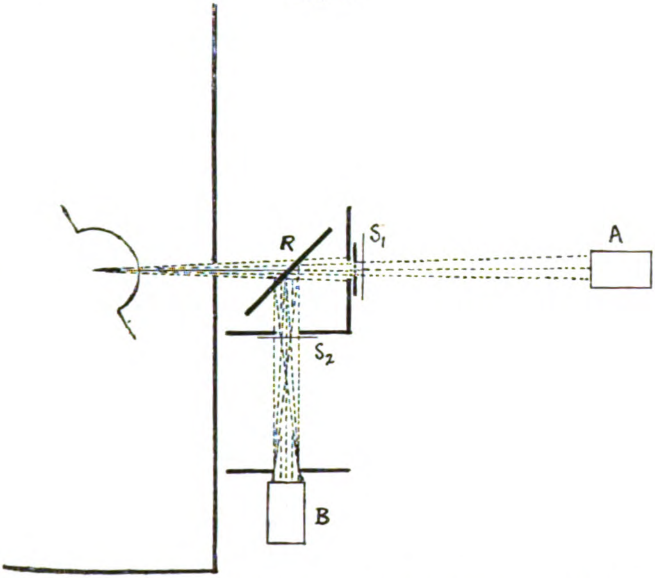
* Phil. Mag. April 1923.

The ratio $\frac{\text{Ionization in B}}{\text{Ionization in A}}$ was determined. Thin similar sheets of aluminium were placed at S_1 and S_2, and the above ratio was observed for each thickness of aluminium.

Fig. 1.



The relation between thickness of aluminium and this ratio is shown in Table I. and is represented graphically in fig. 2.

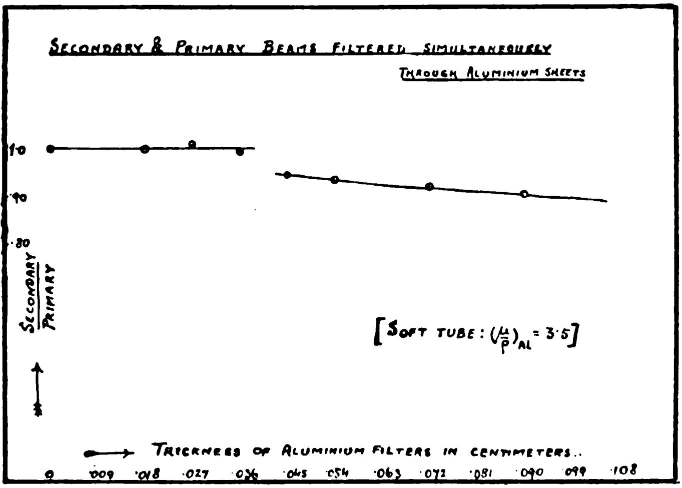
TABLE I.

Soft tube : $\left(\frac{\mu}{\rho}\right)_{\text{Al}} = 3{\cdot}5$ (from 50 per cent. absorption).

Thickness of Al filters.	Observed ratio $\frac{\text{Secondary}}{\text{Primary}}$ (in arbitrary units).
0·0 cm.	1·00 × x
·018 ,,	1·00 ,,
·027 ,,	1·01 ,,
·036 ,,	·99(5) ,,
·045 ,,	·94(5) ,,
·054 ,,	·93(5) ,,
·072 ,,	·92 ,,
·090 ,,	·90(5) ,

With 2, 3, and 4 sheets the ratio remained unchanged, showing a very exact equality in penetrating powers and thus in wave-lengths of the primary and secondary radiations. The fifth sheet (giving a total thickness of ·45 millimetre) produced a very big absorption of the secondary beam, as shown by the ratio suddenly dropping from 1·00 to 0·94(5). Subsequent sheets absorbed the secondary beam more than the primary. This is shown by the steady diminution of the ratio for 5, 6, 8, and 10 sheets. In the graph of fig. 2 the first horizontal portion shows equality of penetrating powers of the secondary and primary; the sudden drop shows the large absorption of energy of the secondary beam, and the slope of the curve to the right shows the transformation which has been produced by transmission through the aluminium. The particular sheet at which the transformation occurs depends upon the original penetrating power of the radiation. With harder radiations the discontinuity is displaced to the left of the figure (see fig. 3 and Table II.), and with softer radiations to the right; for the transformation seems to occur when a certain average penetrating power is reached—in this case by filtering. Indeed, with a more penetrating radiation the discontinuity is lost sight of, for even the first thin sheet of absorbing material shows that the difference between the primary and secondary

Fig. 2.



radiations has already been produced. Under such conditions the true nature of the phenomenon is concealed.

Fig. 3.

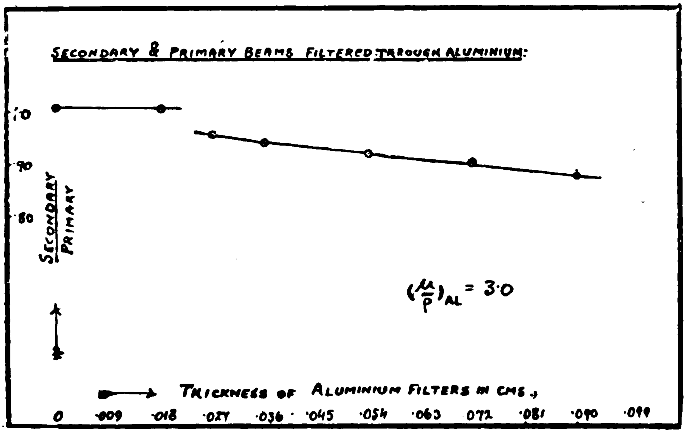


TABLE II.

Soft tube: $\left(\frac{\mu}{\rho}\right)_{Al} = 3$ (from 50 per cent. absorption).

Thickness of Al filters.	Observed ratio $\frac{\text{Secondary}}{\text{Primary}}$ (in arbitrary units).
0·0 cm.	1·01 × x
·018 „	1·00(5) „
…………………	…………………
·027 „	·95(5) „
·036 „	·94 „
·054 „	·92 „
·072 „	·90 „
·090 „	·87(5) „

Similar discontinuities have been obtained by filtering the radiations both by paper and by copper. Fig. 4, plotted from the results of Table III., show the corresponding phenomenon in paper. Experiments show that it is necessary to cut off a little more by aluminium than by paper to give the discontinuity—a result perfectly consistent with the conclusions from experiments of a different kind.

Fig. 4.

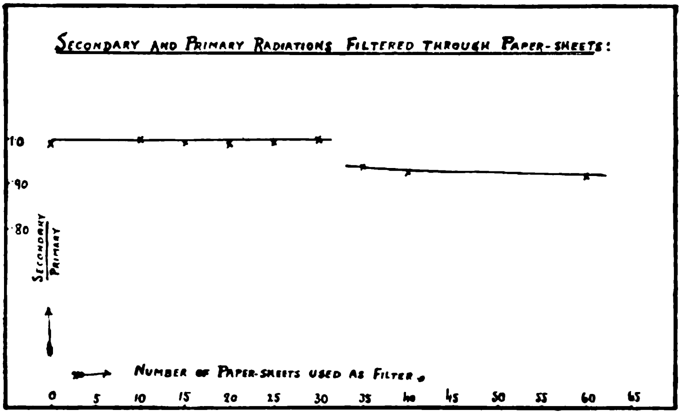


TABLE III.

Soft tube : $\left(\frac{\mu}{\rho}\right)_{\text{Al}} = 3{\cdot}5$ (approx. from 50 per cent. absorption).

Number of Paper-sheets.	$\frac{\text{Secondary}}{\text{Primary}}$ (in arbitrary units).
0	·99 × x
10	1·00 ,,
15	·99(5) ,,
20	·99 ,,
25	·99(5) ,,
30	1·00 ,,
…………………	………………
35	·94 ,,
40	·93 ,,
60	·92 ,,

These are only a few of a very large number of experimental results illustrating the "J" phenomenon. This has been briefly described elsewhere, and is receiving fuller treatment in a series of papers. In the case described above, it was the secondary radiation which exhibited the J phenomenon.

Our present purpose in taking this experimental result from its context is to show that the transformation in the secondary radiation has not been produced in the process of scattering. Scattering followed the classical laws; the J transformation gave the appearance of a change of wave-length in scattering.

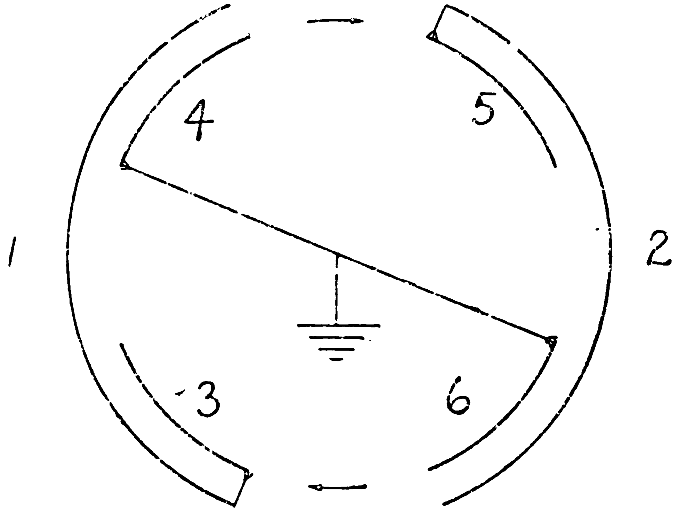
As previously stated, the J process is probably governed by quantum laws—but it is quite distinct and fundamentally different in origin and nature from the process of scattering.

XXVII. *A Quantitative Analysis of a Four Carrier, Voss Machine.* By ALFRED W. SIMON *.

A GENERAL quantitative theory of the influence electrostatic generator has recently been outlined by the author †.

The present work is concerned with the detailed analysis of a very simple electrostatic generator, one which may be taken as the prototype of the Voss or Toepler-Holtz machines. It consists (fig. 1) of six elements: four carriers and two inductors, and operates as follows:—

Fig. 1.



When the elements assume the configuration shown, two of the carriers, namely those in positions 4 and 6, are earthed; while two others, namely those in positions 3 and 5, are connected to the inductors 1, 2. A quarter turn later the two which were previously earthed are connected to the inductors, while the two which were previously connected to the inductors are now earthed.

It is assumed that the carriers are exactly alike and symmetrically mounted, so that a quarter turn brings the whole system again into the same geometrical configuration. In the mathematical treatment of such a machine the individual carriers lose their identity, and it is necessary to consider the electrical coefficients of the elements in only one configuration (that of the figure), irrespective of which carrier, in particular, occupies any one position.

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* Communicated by Prof. A. H. Compton.

† Proc. Nat. Acad. of Sciences, x. p. 302 (1924).

This fact is reflected in our notation, which may now be defined. We shall let q_{1n} represent the charge of the inductor 1 at the beginning of the *n*th cycle (quarter turn) ; q_{2n}, the charge of the inductor 2 at the beginning of the *n*th cycle ; q_{3n} the charge on the carrier *which occupies position* 3 at the beginning of the *n*th cycle ; and so on. Further, we shall let V_{1n} and V_{2n} represent the potentials of the inductors 1 and 2 respectively at the beginning of the *n*th cycle ; V_{1n+1} and V_{2n+1}, the potentials of the inductors 1 and 2 respectively at the beginning of the $(n+1)$st cycle ; and so on.

We then have, according to well-known electrostatic theory, for the *n*th cycle :—

$$\left.\begin{aligned}
q_{1n}&=a_{11}V_{1n}+a_{21}V_{2n}+a_{31}V_{1n}+a_{51}V_{2n},\\
q_{2n}&=a_{12}V_{1n}+a_{22}V_{2n}+a_{32}V_{1n}+a_{52}V_{2n},\\
q_{3n}&=a_{13}V_{1n}+a_{23}V_{2n}+a_{33}V_{1n}+a_{53}V_{2n},\\
q_{4n}&=a_{14}V_{1n}+a_{24}V_{2n}+a_{34}V_{1n}+a_{54}V_{2n},\\
q_{5n}&=a_{15}V_{1n}+a_{25}V_{2n}+a_{35}V_{1n}+a_{55}V_{2n},\\
q_{6n}&=a_{16}V_{1n}+a_{26}V_{2n}+a_{36}V_{1n}+a_{56}V_{2n},
\end{aligned}\right\} \quad . \quad . \quad . \quad (1)$$

and for the $(n\text{th}+1)$st cycle :

$$\left.\begin{aligned}
q_{1n+1}&=a_{11}V_{1n+1}+a_{21}V_{2n+1}+a_{31}V_{1n+1}+a_{51}V_{2n+1},\\
q_{2n+1}&=a_{12}V_{1n+1}+a_{22}V_{2n+1}+a_{32}V_{1n+1}+a_{52}V_{2n+1},\\
q_{3n+1}&=a_{13}V_{1+n1}+a_{23}V_{2n+1}+a_{33}V_{1n+1}+a_{53}V_{2n+1},\\
q_{5n+1}&=a_{15}V_{1+n1}+a_{25}V_{2n+1}+a_{35}V_{1n+1}+a_{55}V_{2n+1},
\end{aligned}\right\} \quad . \quad (2)$$

Further, if we assume no leakage, we can put

$$\left.\begin{aligned}
q_{1n+1}+q_{3n+1}&=q_{1n}+q_{6n},\\
q_{2n+1}+q_{5n+1}&=q_{2n}+q_{4n}.
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (3)$$

In the system of equations (1), (2), (3) there are 12 equations and 14 unknowns ; hence by elimination we can derive two simultaneous equations of the form

$$V_{1n+1}=LV_{1n}-MV_{2n}, \quad . \quad . \quad . \quad . \quad . \quad (4\,a)$$

$$V_{2n+1}=SV_{2n}-RV_{1n}, \quad . \quad . \quad . \quad . \quad . \quad (4\,b)$$

where L, M, R, S are certain functions of the coefficients of induction and coefficients of capacity involved in equations (1).

If we solve (4 *b*) for V_{2n}, we have

$$MV_{2n} = LV_{1n} - V_{1n+1},$$

and, raising the subscripts by unity, we have, further,

$$MV_{2n+1} = LV_{1n+1} - V_{1n+2}.$$

Substituting these values in (4 *a*), we obtain

$$V_{1n+2} - KV_{1n+1} + NV_{1n} = 0, \quad . \quad . \quad . \quad (5\,a)$$

where $K = (L+S)$,

$N = (LS - RM)$,

Similarly, if we eliminate the terms of the V_1 sequence, we obtain

$$V_{2n+2} - KV_{2n+1} + NV_{2n} = 0 \quad . \quad . \quad . \quad . \quad (5\,b)$$

Now, the theory of finite differences * applied to (5 *a*) gives for V_{1n} an equation of the form

$$V_{1n} = C_1 r_1^n + C_2 r_2^n, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6\,a)$$

and applied to (5 *b*), for V_{2n}

$$V_{2n} = C_3 r_1^n + C_4 r_2^n, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6\,b)$$

where r_1, r_2 are the roots of the quadratic equation

$$r^2 - Kr + N = 0,$$

and C_1, C_2, C_3, C_4 are constants, which are to be determined from the initial values of V_{1n} and V_{2n}.

The values of the constants r_1, r_2, C_1, C_2, C_3, C_4, L, M, R, S, obtained by actual solution, are given in Table I.

TABLE I.

$$L = \quad S = (a_{23,\,25}\, a_{25,\,24} - a_{25,\,13}\, a_{25\ 16})\, \Delta,$$

$$-M = -R = (a_{23,\,25}\, a_{23,\,16} - a_{25,\,13}\, a_{25,\,24}) / \Delta,$$

$$\Delta \equiv (a_{23,\,25}\, a_{25,\,25} - a_{25,\,13}\, a_{25,\,13}).$$

$$C_1 = \quad C_3 = (V_{11} + V_{21}) / 2r_1,$$

$$C_2 = -C_4 = (V_{11} - V_{21}) / 2r_2.$$

$$r_1 = (a_{25,\,24} + a_{25,\,16}) / (a_{25,\,25} + a_{25,\,13}),$$

$$r_2 = (a_{25,\,24} - a_{23,\,16}) / (a_{25,\,25} - a_{25,\,13}).$$

$$r_2 - L = M = R = r_2 - S,$$

$$r_1 - L = -M = -R = r_1 - S,$$

$$r_2 - r_1 = 2M = 2R.$$

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* G. Boole, 'A Treatise on the Calculus of Finite Differences,' Chapter 11.

The notation employed in this table requires a word of explanation. It will be noted that expressions of the form $a_{pq,rs}$ occur. These are defined by $a_{pq,rs}=a_{pr}+a_{ps}+a_{qr}+a_{qs}$.

The physical significance of these expressions, as Maxwell * has pointed out, is that they are the electrical coefficients of pairs of bodies: for example, $a_{25,25}$ represents the coefficient of capacity of the bodies 2 and 5, in this case *connected together* ; $a_{25,13}$ the coefficient of induction of the pair 25 and the pair 13 ; etc.

Selecting r_1 for further analysis, it can be proved that

$$-1<r_1<+1.$$

In order to show that r_1 is less than $+1$, let us write it in the form

$$r_1=\frac{1+\dfrac{a_{25,6}+a_{25,4}}{a_{25,1}+a_{25,2}}}{1+\dfrac{a_{25,3}+a_{25,5}}{a_{25,1}+a_{25,2}}}.$$

Now we know from the properties of the coefficients that

$$\left.\begin{aligned} a_{25,6}+a_{25,4}&<0,\\ a_{25,1}+a_{25,2}&>0,\\ a_{25,3}+a_{25,5}&>0.\end{aligned}\right\} \quad \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \quad (7)$$

Hence r_1 must be less than unity.

The first of the inequalities (7) follows directly from the fact that every coefficient of induction is negative. The second of the inequalities can be proved as follows :—

$$a_{25,1}+a_{25,2}=a_{21}+a_{51}+a_{22}+a_{52}\ ;$$

but, since the machine is symmetrical, $a_{51}=a_{23}$, so that our expression becomes

$$a_{25,1}+a_{25,2}=a_{22}+a_{21}+a_{23}+a_{25}\ ;$$

and this is positive, since

$$a_{22}>(a_{21}+a_{23}+a_{25}).$$

The third inequality can be established in a similar manner, for $(a_{25,3}+a_{25,5})$ can be written in the form

$$\begin{aligned} a_{25,3}+a_{25,5}&=a_{23}+a_{53}+a_{25}+a_{55}\\ &=a_{55}+a_{15}+a_{25}+a_{35}\ ;\end{aligned}$$

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* J. C. Maxwell, 'A Treatise on Electricity and Magnetism,' i. p. 110, 3rd ed. (1892).

and this is positive, since

$$a_{55} > |a_{15} + a_{25} + a_{35}|.$$

In order to show that r_1 is greater than -1, we proceed as follows :—If r_1 is less than or equal to -1, we have

$$\frac{a_{25,16} + a_{25,24}}{a_{25,13} + a_{25,25}} \overset{=}{<} -1\,;$$

that is, $$a_{25,16} + a_{25,24} + a_{25,13} + a_{25,25} \overset{=}{<} 0.$$

If this inequality is to be satisfied, we must have

$$A + B + C \overset{=}{<} 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

where
$$A = a_{22} + a_{21} + a_{23} + a_{24} + a_{25} + a_{26},$$
$$B = a_{22} + a_{21} + a_{23} + a_{25},$$
$$C = a_{55} + a_{15} + a_{25} + a_{35} + a_{45} + a_{65}\,;$$

but all the quantities A, B, C are positive and greater than zero, so that the inequality (8) cannot be true. Hence r_1 cannot be less than or equal to -1.

A similar analysis shows that r_2 lies in the range

$$-1 < r_2 < +\infty.$$

Summarizing the results obtained so far, we have

$$\left.\begin{array}{l} V_{1n} = (V_{11} + V_{21}) r_1{}^n / 2r_1 + (V_{11} - V_{21}) r_2{}^n / 2r_2, \\ V_{2n} = (V_{11} + V_{21}) r_1{}^n / 2r_1 - (V_{11} - V_{21}) r_2{}^n / 2r_2, \\ \quad n = 1, 2, 3, \ldots. \\ \quad -1 < r_1 < +1, \qquad -1 < r_2 < +\infty. \end{array}\right\}. \qquad (10)$$

From equations (10) a number of important conclusions can be drawn :—

First, it is seen that the terms in $r_1{}^n$ represent *transient terms*, which vanish for large values of n and are absent altogether, provided the potentials of the inductors are equal and opposite to begin with.

Secondly, if $r_2 > 1$, and this is the case in practice, the potentials of the inductors eventually become equal and opposite, and approach infinity as n approaches infinity.

Thirdly, for the case $r_2 > 1$, $r_1 < 0$ we have an *oscillatory* transient term, since the potential of the inductor then satisfies the equation

$$V_{1n}=C_1(-\rho_1)^n+C_2 r_2^n, \qquad \rho_1 \equiv | r \quad ,$$

$(-\rho_1)^n$ being alternately positive and negative.

Finally, it is evident that r_2 is the ratio by which the potential of the inductors increases per quarter revolution.

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XXVIII. *On the Incident and Emergent Velocities of Photo-Electrons emitted from Thin Platinum Films.* By CHIEN CHA, *Ph.D.* *

Introduction.

IT is well known that Röntgen rays and γ rays, on passing through thin films, produce different ionization effects on the two sides. A similar asymmetry has been observed in the numbers and velocities of photo-electrons emitted from the two sides of a thin film. The present work deals with the velocities of these electrons only. The side of a thin film upon which light falls will be referred to as the incident side, and the other side will be referred to as the emergent side.

J. Robinson † investigated the velocities of photo-electrons emitted by a thin platinum film on the incident and on the emergent side. He found that for very thin films (less than 10^{-7} cm.) the maximum velocity of emission due to emergent light was greater than that due to the incident; for thicker films the reverse was found to be true. In his first paper he gave 1·24 and in his second paper 1·12 as the maximum value for the ratio of emergent to the incident velocities. The same question was taken up by O. Stuhlmann, Jr. ‡ at a later date. He confirmed Robinson's results except in so far as the ratios given by Stuhlmann were a little larger.

Neither the electromagnetic theory of light nor the quantum theory indicates any asymmetry of a measurable order in the photo-electric effect. Richardson § and Swann ‖ independently investigated the matter from the quantum theory in slightly different forms, and Swann also investigated it from the classical electromagnetic theory. In all cases, the order of magnitude of the asymmetry predicted is far below that of the asymmetry actually observed.

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* Communicated by Prof. W. F. G. Swann. Presented at the Christmas meeting of the American Physical Society, December 1923.

† Phil. Mag. xxiii. p. 542 (1912); Pt. II., Phil. Mag. xxv. p. 115 (1913).

‡ Phys. Rev. iv. p. 195 (1914).

§ Phil. Mag. xxv. p. 144 (1913).

‖ Phil. Mag. xxv. p. 534 (1913).

In the works of Robinson and Stuhlmann cited above, the films used were produced by means of cathode sputtering. Also, the ultra-violet light was furnished by a quartz mercury lamp and was unresolved. The results thus obtained could not be used to decide whether or not the effect under investigation has any fundamental significance, because it is quite conceivable that the conditions under which the experiments were carried out might have impressed upon the results this observed peculiarity. It would then seem to be in the interest of more precise information to have the phenomenon re-investigated with unresolved light as well as monochromatic light, with sputtered films as well as evaporated films.

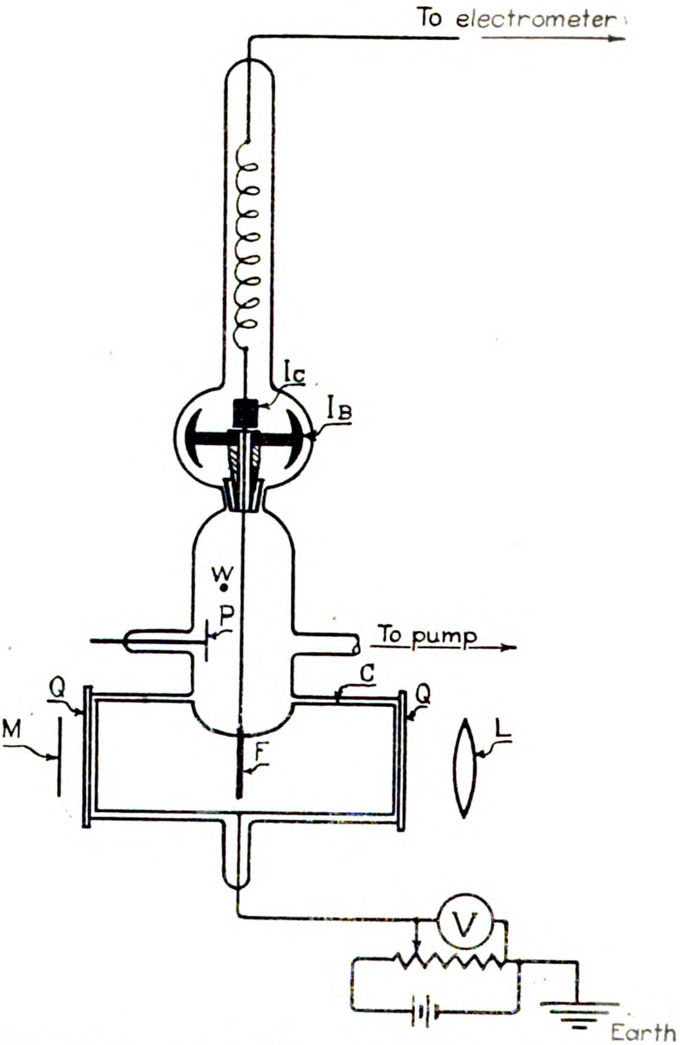
Experimental Arrangement and Method.

Figure 1 gives a diagrammatic representation of the apparatus used in the present experiment. It was made of glass with two quartz windows Q for the admission of ultra-violet light. F is a quartz plate upon which platinum films were deposited. P is a platinum plate for the purpose of sputtering, and W a platinum wire for the purpose of depositing films by evaporation. I_C is an iron cylinder. I_B are two iron bars with hemispherical attachments at the ends. The iron cylinder and bars were operated by electromagnets not shown in the figure for the purpose of lifting and turning the plate F respectively. C is an aluminium cylinder, the potential of which could be altered by means of a potentiometer system. L is a condensing quartz lens. M is a mirror silvered on the surface.

The process of obtaining an evaporated film was as follows :—The wire W was heated to a white heat by passing a current through it. Then the quartz plate F was lifted into a position directly opposite the plate P by means of an electromagnet operating on the iron cylinder I. The electromagnet, being made to move up and down along the upper portion of the tube by the rotation of an eccentric cam, in turn caused the plate to move up and down in front of the hot wire while evaporation was going on. This vertical motion of the plate extending over a distance of about 7 cm. was necessary in order to make sure of the uniformity of the resulting film.

To obtain a sputtered film, the plate P was connected to the negative pole of a high tension battery, the cylinder C was connected to the positive pole and the quartz plate F was lifted into a position directly opposite the plate P. All sputtered films used were obtained at a pressure of

Fig. 1.



·003 mm. of mercury, with a potential difference of 900 volts and a current of 20 milliamperes.

A quartz mercury lamp was used as the source of light. When unresolved light was used, a narrow beam of it was allowed to fall on the quartz lens L which focussed it through the film on the mirror M. The latter in turn reflected the light back on to the film. With this arrangement, the images on the film due to the primary and the reflected beam were of the same size. Monochromatic light was obtained by means of a Hilger monochromatic illuminator. It was focussed as in the case of unresolved light.

Measurements of the maximum potential to which the film was raised as a consequence of the emission of photo-electrons were made by applying a negative potential to the aluminium cylinder C such that only potential less than 1/100 of a volt was left to be indicated by the deflexion of the electrometer. The reading of a voltmeter included in the potentiometer circuit, added to the deflexion of the electrometer in terms of volts, gave the true potential of the film. In each reading taken, light was first shut off from the mirror M until the electrometer had attained its full deflexion and then was allowed to fall on the mirror. Any consequent change in the deflexion was a measure of the difference of the incident and emergent velocities of electrons emitted from the film. The film was then turned through an angle of 180° by means of an electromagnet operating on the iron bars I so that the quartz side was facing the lens L, and a similar reading was taken.

A liquid air vacuum was maintained in the apparatus throughout the course of the experiment except when sputtered films were being made. Evaporated films were made and kept in liquid air vacuum.

Results with Evaporated Films.

It is customary to express the velocity of an electron in terms of the potential that has to be applied in order to stop its motion. The velocity v and the potential V are connected by the relation :

$$\tfrac{1}{2}mv^2 = e\mathrm{V},$$

where m is the mass and e the charge of the electron.

Table I.* gives the average readings obtained with monochromatic light, for different wave-lengths. All the data in this table refer to cases where the primary beams of light fell upon the film side of the plate. They clearly show that the asymmetry of velocities, which was looked for in the experiment, is absent if the film is obtained by evaporation.

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* The apparent absolute agreement of the readings for mirror on and mirror off simply indicates that the mirror caused an alteration of the electrometer deflexion corresponding to less than 0·001 volt in each case.

TABLE I.

(Monochromatic Light : Evaporated Films.)

Time of Deposit (in min.).	Potentials measuring Maximum Emission Velocities (in volts).					
	$\lambda=2537$ Å.		$\lambda=2150$ Å.		$\lambda=1849$ Å.	
	Mirror off.	Mirror on.	Mirror off.	Mirror on.	Mirror off.	Mirror on.
3	0·510	0·510	1·423	1·423	2·281	2·281
4·5	0·508	0·508	1·420	1·420	2·282	2·282
6	0·511	0·511	1·419	1·419	2·280	2·280

Furthermore, these readings show that this absence of asymmetry is independent of the thickness of film and the wave-length of light over the range covered by the experiment.

When this result was first obtained, it was feared that the amount of light reflected back on to the film by the mirror M, which was supposed to be responsible for the emergent photo-electric effect, might not have been sufficient to give rise to any measurable photo-electric effect. In other words, it was feared that the intensity of light might have been very greatly reduced by the reflexion, and absorption in the film. Therefore a set of readings of the photo-electric current was taken after every set of readings of the photo-electric potentials. The current readings corresponding to the potential readings of Table I. are given in Table II. In the latter table, the current reading obtained when the mirror M was shut off is taken to be unity for each particular thickness of film and also for each particular wave-length of light. The readings clearly show that the amount of light reflected back on to the film in each case is amply sufficient for the production of a photo-electric effect. Consequently, if the emergent velocity were greater than the incident velocity, this effect should have manifested itself in the measurements of Table I.

TABLE II.

(Monochromatic Light : Evaporated Films.)

Time of Deposit (in min.).	Relative Magnitude of the Photo-Electric Current.					
	$\lambda=2537$ Å.		$\lambda=2150$ Å.		$\lambda=1849$ Å.	
	Mirror off.	Mirror on.	Mirror off.	Mirror on.	Mirror off.	Mirror on.
3	1	1·65	1	1·64	1	1·62
4·5	1	1·52	1	1·49	1	1·50
6	1	1·36	1	1·35	1	1·36

There is, however, left another possibility. We remarked in the earlier part of this paper that Robinson found, for films thicker than 10^{-7} cm., the ratio of emergent to incident velocities to be less than unity. Owing to the particular manner in which the readings recorded in Table I. were obtained, any emergent velocity, if smaller than the incident velocity, would not have a chance to influence the electric potential measured. Although the thickness of the films used was decidedly less than 10^{-7} cm. and so could not give the ratio of emergent to incident velocity less than unity according to Robinson's results, nevertheless it was thought desirable to repeat the experiment in such a way as to remove definitely even this improbable possibility. The film was consequently turned through an angle of 180° so that the quartz side was facing the condensing lens, and a set of readings similar to those of Table I. was taken. These readings are given in Table III., and they are identical with those in Table I. within the limit of observational error.

TABLE III.

(Monochromatic Light : Evaporated Films.)

Potentials measuring Maximum Emission Velocities (in volts).

Time of Deposit (in min.).	$\lambda=2537$ Å.		$\lambda=2150$ Å.		$\lambda=1849$ Å.	
	Mirror off.	Mirror on.	Mirror off.	Mirror on.	Mirror off.	Mirror on.
3 …………	0·509	0·509	1·421	1·421	2·279	2·279
4·5 …………	0·513	0·513	1·418	1·418	2·282	2·282
6 …………	0·512	0·512	1·422	1·422	2·284	2·284

In Table IV. are recorded the measurements made with evaporated films when unresolved light was used. Since the line of shortest wave-length present in the light used was probably 1849 Å, these readings really give the potentials due to that line. The readings enclosed in parentheses were in fact taken with the line 1849 A°. The excellent agreement which they show with the readings actually obtained with unresolved light testifies to the soundness of our statement above. Just as the use of the line 1849 Å did not give rise

TABLE IV.

(Unresolved Light : Evaporated Films.)

Potentials measuring Maximum Emission Velocities (in volts).

Time of Deposit (in min.).	Mirror off.	Mirror on.
3 ……………	(2·281)	(2·281)
4·5 ……………	(2·282)	(2·282)
6 ……………	2·280	2·280
7·5 ……………	2·278	2·278

to any lack of symmetry in the velocities of the photo-electrons, so the use of unresolved light did not disclose the effect which was looked for in the experiment.

Calculation of Planck's Constant "h."

Although the purpose of the present investigation was not the determination of Planck's constant, it was thought to be interesting to find out whether or not the correct value of "*h*" could be calculated from the results obtained. This procedure would serve as a good test of the reliability of the experiment.

The photo-electric effect was among the first effects to which the quantum theory was applied. The following relation connecting the maximum emission energy of a photo-electron and the frequency of the light causing its emission was proposed by Einstein in 1905 and is known as Einstein's equation :

$$Ve=h\nu-w.$$

where e is the electronic charge, ν the frequency of light, h Planck's constant, V the difference of potential necessary to stop the electron, and w the energy lost in getting out of the substance. Stated in words, this means that the energy of a photo-electron ejected from a substance by light of frequency ν is equal to the energy associated with a quantum of light of that frequency, namely, $h\nu$, less the loss of energy in getting out of the substance. There are several important implications of the equation, and two of them can be stated as follows:

(1) The energy of a photo-electron is a linear function of the frequency of light.

(2) The slope of the line connecting the energy and the frequency is the well-known quantum constant "*h*."

For a time it was thought by some investigators that the photo-electrons from thin films had necessarily high emission velocities. Stuhlmann and Compton * found that there was no departure from Einstein's law, provided adequate care were taken to prevent the formation of charged layers, apparently due to the presence of soft wax or grease inside the apparatus where the film was sputtered.

At the time when Robinson and Stuhlmann published their result that the maximum emission energy of the photo-electrons from a thin film was greater when they left the emergent side, the investigations of the emission energies of photo-electrons from ordinary surfaces all led to values of "*h*" about 10 per cent. or 20 per cent. too low. It was therefore suggested that the correct value for "*h*" might be obtained if the velocities were measured for the emergent side. In view of the later experiment by Millikan * on the incident velocities of the photo-electrons from which "*h*" was accurately obtained, the above explanation can no longer be maintained.

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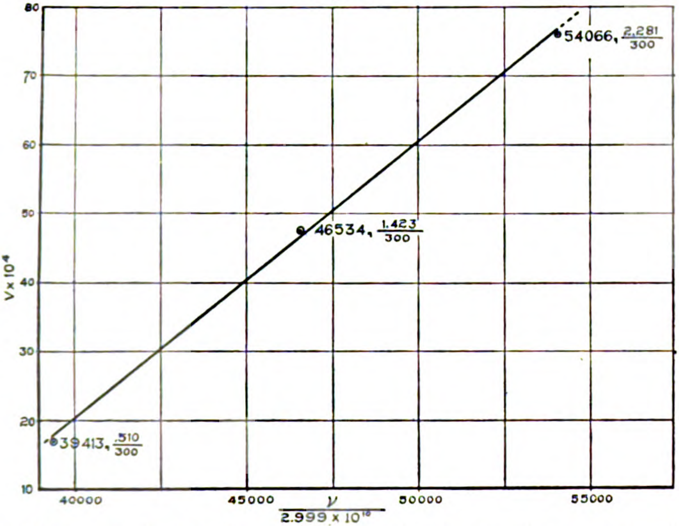
* Phys. Rev. ii. p. 199 (1913) ; ii. p. 2327 (1913).

The curve in fig. 2 was plotted with the readings recorded in Table I. for the film whose time of deposit is 3 minutes. Since the readings for the other films are practically the same as those used, the curves due to them are not included here. It is clear that, over the range covered by the present experiment, the maximum emission energy of a photo-electron emitted from a thin evaporated film is a linear function of the frequency of light.

Fig. 2.



The curve in fig. 2 was plotted with the maximum potential in e.s.u. against the frequency of light. If Einstein's equation holds in this case, the slope of the line should be equal to h/e, where h denotes Planck's constant and e denotes the electronic charge. The value of this slope can of course be measured directly from the graph. But it was thought desirable to obtain it in a little different way. A straight line was drawn through every possible pair of points and the slope of the line was calculated. The mean of these slopes was then taken to be the slope of the line representing all the points. Its value is $\frac{403}{2{\cdot}999} \times 10^{-19}$. Taking

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* Phys. Rev. vii. p. 355 (1916).

Millikan's value of e, which is $4{\cdot}774 \times 10^{-10}$ e.s.u., we obtain, for the value of Planck's constant,

$$h = \frac{403}{2{\cdot}999} \times 10^{-19} \times 4{\cdot}774 \times 10^{-10} \text{ erg. sec.}$$

$$= 6{\cdot}415 \times 10^{-27} \text{ erg. sec.}$$

Comparing this with the value of "h" given by Millikan, namely, $6{\cdot}547 \times 10^{-27}$, the value calculated from the present experiment is about 2 per cent. too low. In view of the fact that the experimental error is probably of this order of magnitude, it is believed that no better agreement can be expected.

Results with Sputtered Films.

In Table V. are recorded the potentials corresponding to the maximum emission velocities of photo-electrons from sputtered films when monochromatic light was used. Here appears distinctly the asymmetry of emission velocities which was absent in the case of evaporated films. Two other points are also noticeable. First, over the range of the present experiment, the ratio E/I decreases with the increase of the thickness of the film. The form of the curve representing this variation is given in fig. 3. Secondly, over the range of wave-lengths used in the experiment, the ratio E/I stays practically constant.

Table V.—(Monochromatic Light: Sputtered Films.)

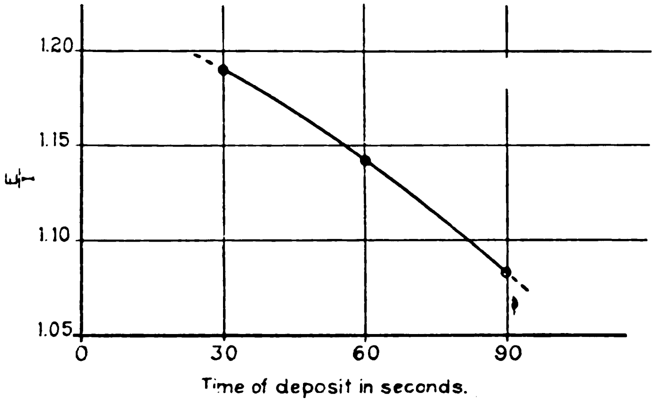
		Time of Deposit (in sec.)	30	60	90
Potentials Measuring Maximum Emission Velocities (in volts).	2537 Å.	Mirror off (I)	0·524	0·553	0·585
		Mirror on (E)	0·630	0·634	0·640
		E/I	*1·20*	*1·15*	*1·09*
	2150 Å.	Mirror off (I)	1·412	1·455	1·524
		Mirror on (E)	1·669	1·654	1·630
		E/I	*1·18*	*1·14*	*1·07*
	1849 Å.	Mirror off (I)	1·915	1·984	2·077
		Mirror on (E)	2·278	2·265	2·271
		E/I	*1·19*	*1·14*	*1·09*

Table VI. gives the potentials corresponding to the maximum emission velocities of photo-electrons obtained with unresolved light. As in the case of evaporated films, the readings due to the line 1849 Å are here tabulated with the readings due to unresolved light, it being assumed that the line 1849 Å was probably the line of shortest wave-length present in the unresolved light used, and consequently the line responsible for the resulting potential of the film. Here, again is observed a distinct asymmetry of velocities. Also,

Table VI.—(Unresolved Light : Sputtered Films.)

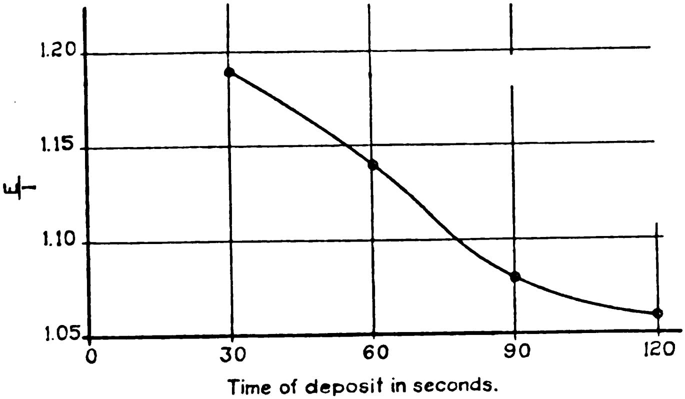
Time of Deposit (in sec.).	Potentials measuring Maximum Emission Velocities (in volts).		
	Mirror off (I).	Mirror on (E).	E/I.
30 …………	(1·915)	(2·278)	*(1·19)*
60 …………	(1·984)	(2·265)	*(1·14)*
90 …………	2·105	2·273	*1·08*
120 …………	2·142	2·271	*1·06*

Fig. 3.



the ratio E/I decreases with the thickness of the film. The form of this variation is shown in fig. 4.

Fig. 4.



It may be mentioned in this connexion that the form of the curves in figures 3 and 4 representing the variation of the ratio of the emergent to incident velocity with the thickness of film is in accord with the results given by Robinson and Stuhlmann.

Discussion.

All the data presented in this paper point unmistakably to the conclusion that the observed asymmetry of velocities of photo-electrons is due to some fundamental difference or differences existing between a sputtered film and an evaporated film. A more thorough study of the properties of these two types of films than has so far been made, will undoubtedly be of great value to the formulation of an adequate explanation. One thing, however, is clear, that is, the fact that while evaporation is done in the best vacuum possible, sputtering requires a fairly high pressure. This immediately leads to the possibility that the residual gases which are occluded or absorbed by the particles of matter during the process of sputtering may be chiefly responsible for the subsequent lack of symmetry which is observed on the maximum velocities of the photo-electrons emitted by the film. If in addition we make the assumption that photo-electrons are shot out from their systems in the direction of the light, it seems obvious that electrons due to the incident light, in order to come out on the film side, will have to describe orbits within the film, thus travelling a greater distance through the film and consequently through the occluded gases than electrons due to the emergent light. Just what the electrons do when they travel through the occluded gas is not known, but it is reasonable to suppose that they suffer a loss of velocity. This would account for the excess of the emergent over the incident velocity.

It is of course not practicable to base any conclusions on a comparison of the absolute velocities of the electrons emitted from evaporated and sputtered films, as the work function may be quite different for the two cases.

A rather remarkable result is found if we plot the maximum velocity against the frequency for sputtered films. Instead of obtaining a linear relation as in the case of evaporated films, we obtain curves departing far from linearity, so that it would be impossible to attach any significance to the calculation of "*h*" from the results for sputtered films. The non-linearity of the curves suggests that both in the case of the electrons emitted by incident light and also in that of the electrons emitted by emergent light, the loss of energy in passing through the occluded gases in the process of escape from the surface is a function of the velocity of the electron.

The investigation described in this paper was carried out under the direction of Professor W. F. G. Swann, at the University of Minnesota, and the writer desires to express his deep appreciation to Professor Swann for the very kind advice and encouragement which he extended throughout the course of the work.

Department of Physics,
University of Minnesota.

XXIX. *A Gyro Compass incorporating two Gyroscopes.*

By Professor Sir JAMES B. HENDERSON, *D.Sc.**

THE gyroscopic compass is a scientific instrument of the most sensitive kind and is an excellent example of the application of theory in practice. It can be so designed that the action of the compass under all conditions can be calculated to a high degree of accuracy so that before the instrument is constructed its behaviour under any circumstances can be foretold, and when the design has materialised the problem then becomes one of locating and eliminating the causes of any differences between the actual and the theoretical behaviour.

During the last ten years the most important problem in gyro compasses has been the elimination of the deviation of the compass introduced by the oscillations of the ship due to wave motion; and when the history of this period comes to be written, an important phase of development will be that in which the compass comprised two gyroscopes. One such compass made by the Sperry Gyroscope Company had one of the gyroscopes meridian-seeking and the other the reverse, but the latter was compelled by discontinuous torques to follow the former. In another two-gyro compass made by the author both gyroscopes were meridian-seeking, all torques being continuous functions and the interaction of the two gyroscopes providing mutual damping. The mathematical analysis of the motion of this latter compass, the conditions for its stability, and the investigation of the damping coefficients of both periods form the subject of this paper.

Description of the Compass.

Fig. 1 represents diagrammatically a front elevation of the compass without its supports or following motor, and fig. 2 represents a side elevation of the sensitive element alone.

The compass contains two gyroscopes A and A′, supported respectively upon horizontal trunnion axes B and B′ in vertical gimbal rings C and C′ pivoted on the vertical trunnions V and V′ in the frame D. This frame is pivoted on the vertical trunnion U in the follower Z. The follower is supported in a binnacle on a large ball race by the disk E which is toothed on its periphery and is driven in azimuth by a small motor controlled by a roller contact F carried by the frame D of the sensitive element and engaging with a two-part commutator G fixed to the follower Z. The following motor therefore keeps the follower Z in phase in azimuth with the roller contact F. The frame D is suspended from the bridge R carried by the plate E by the filar suspension S; the ring C is suspended from the frame D by the torsion element H, and the ring C′ is supported from the frame D by the torsion element H′ which is in thrust.

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* Communicated by the Author.

Fig. 1.

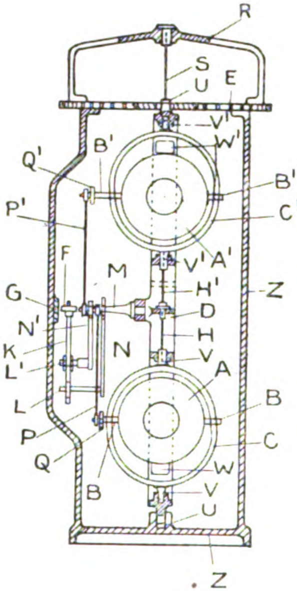
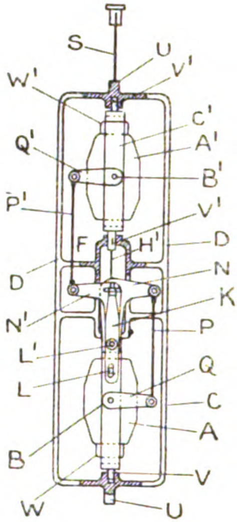


Fig. 2.



The gyroscope A is put in gravitational stability by the weight W, and the gyroscope A′ is put into gravitational instability by the equal weight W′. The main idea in the design is to get an arrangement in which the gravitational control is practically neutral for periodic accelerations of short period due to waves, which is the case if the gyroscope cases A and A′ carrying the weights W and W′ are connected together by a viscous element. The details of this arrangement are omitted in the diagram in order to prevent complication. The gyroscope A′, if acting alone, oscillates about the meridian with its axis of angular momentum pointing South, and in order to damp these oscillations energy has to be supplied to the gyroscope by couples about the vertical axis *assisting* the precession. The gyroscope A, if acting alone, oscillates about the meridian with its axis of angular momentum pointing North, and to damp these oscillations energy has to be taken from the gyroscope by couples acting about the vertical axis *opposing* the precession. Hence a mutual torque between the two gyroscopes due to the torsion elements H and H′ will assist in damping the oscillations of both gyroscopes if the stable gyroscope A precesses faster than the unstable one A′, *i. e.* if A has smaller angular momentum than A′.

With such a combination there would evidently be a stable state with A and A′ in the same azimuth and therefore producing no twist in the filar H–H′ and with A′ tilted more than A so that both precessed in azimuth at the same rate, in which condition they might precess together continuously round and round in azimuth. In order to prevent such a stable state from arising, an external torque with a vertical axis is applied to both gyroscopes proportional to the difference between the tilts of the two rotor axes and in such a direction as to tend to keep the axes of A and A′ in phase as regards tilt. This torque is produced by displacing the roller contact F in azimuth by an amount proportional to the difference in tilt between the two gyros. Horizontal cranks Q and Q′ are fixed to the trunnions B and B′ of the gyros A and A′ (fig. 2), and these are connected by connecting rods P and P′ with two bell-cranks N and N′ pivoted on a spindle M carried by the frame D, so that the bell-cranks N and N′ tilt in phase with the two gyros. The roller contact F is mounted on a lever K which is pivoted on a crank-pin L′ fixed to the bell-crank N′, and a crank-pin L on the bell-crank N engages with a slot in the end of the lever K. It will be evident that this mechanism displaces the roller F in azimuth by an amount proportional to the difference of tilt of the two gyros, and by actuating the following motor twists the suspension S by an amount proportional to the difference in tilt of the two gyroscopes in the direction required to reduce that difference.

Equations of Motion.

Let θ_1 be the azimuthal deviation of gyro A
θ_2 ,, ,, ,, gyro A′
reckoned +ive from N. to W.

ϕ_1 the tilt of gyro A reckoned +ive with N. end high.
ϕ_2 ,, gyro A′ ,, ,, ,,
$G\phi_1$ the gravitation torque on gyro A due to tilt ϕ_1.
$G\phi_2$,, ,, ,, gyro A′ ,, ϕ_2.
$h(\theta_1-\theta_2)$ mutual torque due to torsion element H–H′.
$n(\phi_1-\phi_2)$ torque on both gyros applied externally through suspension.

$I_1\Omega_1$ angular momentum of gyro A.
$I_2\Omega_2$,, ,, ,, gyro A′.
ω_1 angular velocity of precession of gyro A
ω_2 ,, ,, ,, ,, gyro A′
due to unit couple.

ω angular velocity of the earth.

λ latitude.

ω_1 and ω_2 are introduced to avoid reciprocals in the equations.

$$\omega_1 = \frac{\text{unit couple}}{I_1\Omega_1} \quad \text{and} \quad \omega_2 = \frac{\text{unit couple}}{I_2\Omega_2}.$$

It is most convenient to refer the motion of the gyroscopes to axes which move with the rings C and C′. Thus in figs. 3 and 4, which refer respectively to the gyroscopes A and A′, OB represents the horizontal trunnion axis B, OV represents the vertical trunnion axis V, and OX is perpendicular to both and represents the azimuth of the rotor axis OA. OM represents the meridian, and OP is a vector parallel to the axis of the earth and represents the angular velocity of the earth. The angle MOX is θ_1, AOX is ϕ_1, and POM is λ the latitude.

Writing down on each axis the component angular momentum, the component couple, and the component precessional velocity, and equating the couples to the rate of increase of the component angular momentum, assuming θ and ϕ to be small angles, we get from fig. 3:

$$G\phi_1 = I_1\Omega_1(\omega \sin\lambda + \dot{\theta}_1) - I_1\Omega_1\phi_1\omega\cos\lambda,$$

$$h(\theta_2-\theta_1) + n(\phi_2-\phi_1) = I_1\Omega_1\dot{\phi}_1 + I_1\Omega_1\omega\cos\lambda\,.\,\theta_1;$$

Fig. 3.

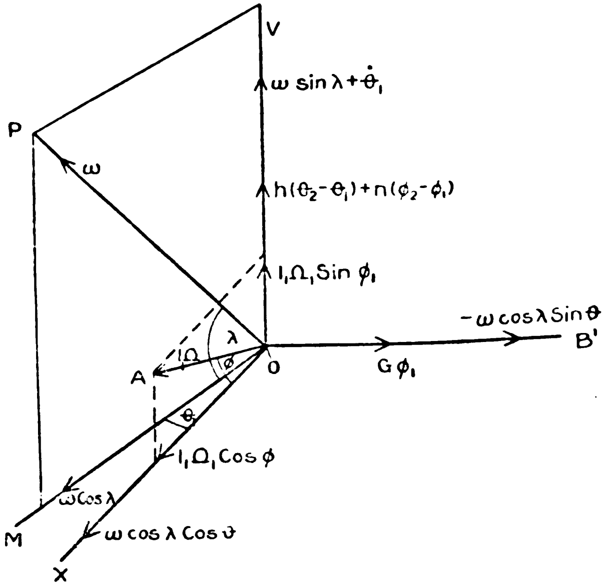
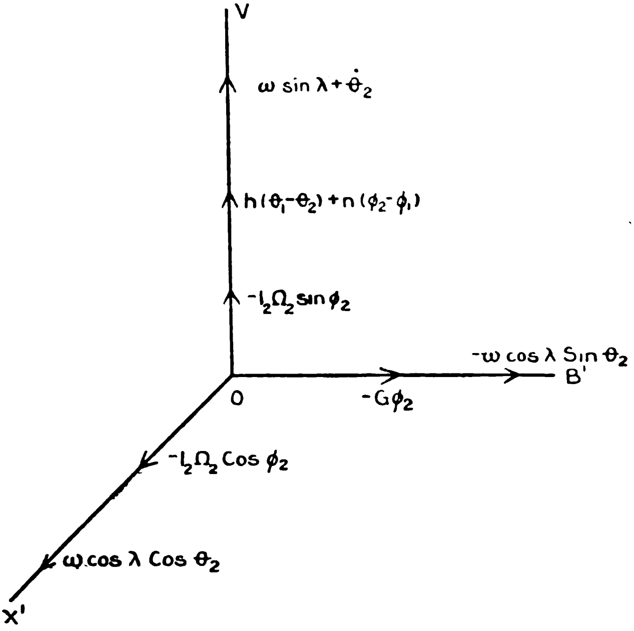

V
$\omega \sin\lambda + \dot{\theta}_1$
P
ω
$h(\theta_2 - \theta_1) + n(\phi_2 - \phi_1)$
$I_1\Omega_1 \sin\phi_1$
$-\omega\cos\lambda\sin\theta$
B'
λ
$I\Omega$
ϕ
A
O
$G\phi_1$
θ
$I_1\Omega_1\cos\phi$
$\omega\cos\lambda$
M
$\omega\cos\lambda\cos\vartheta$
X

Fig. 4.


V
$\omega \sin\lambda + \dot{\theta}_2$
$h(\theta_1 - \theta_2) + n(\phi_2 - \phi_1)$
$-I_2\Omega_2 \sin\phi_2$
$-\omega\cos\lambda\sin\theta_2$
B'
O
$-G\phi_2$
$-I_2\Omega_2\cos\phi_2$
$\omega\cos\lambda\cos\theta_2$
X'

and from fig. 4 :

$$-G\phi_2 = -I_2\Omega_2(\omega \sin\lambda + \dot{\theta}_2) + I_2\Omega_2\phi_2\omega\cos\lambda,$$

$$h(\theta_1-\theta_2) + n(\phi_2-\phi_1) = -I_2\Omega_2\dot{\phi}_2 - I_2\Omega_2\,\omega\cos\lambda\,.\,\theta_2.$$

Whence

$$\left.\begin{aligned}
\dot{\theta}_1 &= \phi_1[G\omega_1 + \omega\cos\lambda] - \omega\sin\lambda,\\
\dot{\theta}_2 &= \phi_2[G\omega_2 + \omega\cos\lambda] - \omega\sin\lambda,\\
\dot{\phi}_1 &= -\omega\cos\lambda\,.\,\theta_1 - h\omega_1(\theta_1-\theta_2) - n\omega_1(\phi_1-\phi_2),\\
\dot{\phi}_2 &= -\omega\cos\lambda\,.\,\theta_2 - h\omega_2(\theta_1-\theta_2) + n\omega_2(\phi_1-\phi_2).
\end{aligned}\right\} \quad . \quad (1)$$

Let

$$\theta_1+\theta_2 = \alpha, \quad \theta_1-\theta_2 = \beta, \quad \phi_1+\phi_2 = \gamma, \text{ and } \phi_1-\phi_2 = \delta.$$

Let $\omega_1+\omega_2 = s$ and $\omega_1-\omega_2 = d$,

then by substitution we get

$$\left.\begin{aligned}
\dot{\alpha} &= G\left(\frac{\gamma}{2}s + \frac{\delta}{2}d\right) - 2\omega\sin\lambda,\\
\dot{\beta} &= G\left(\frac{\gamma}{2}d + \frac{\delta}{2}s\right),\\
\dot{\gamma} &= -\omega\cos\lambda\,.\,\alpha - hs\beta - nd\delta,\\
\dot{\delta} &= -\omega\cos\lambda\,.\,\beta - hd\beta - ns\delta.
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (2)$$

The term $\omega\cos\lambda$ has been omitted in comparison with $G\omega_1$. In the ordinary single-gyro compass $G\omega_1$ is $\dfrac{2\pi}{3 \text{ minutes}}$ whereas $\omega\cos\lambda$ is $\dfrac{2\pi}{48 \text{ hours}}$ at $\lambda = 60°$, and the latter is negligible in comparison with the former. α is of course double the mean deviation of the two gyros, β is their relative motion in azimuth, γ is double the mean tilt, and δ is their relative tilt.

To find the settling position $\dot{\alpha}=\dot{\beta}=\dot{\gamma}=\dot{\delta}=0$ and denote zero value by the suffix $_0$, or more directly in equations (1) let

$$\dot{\theta}_1 = \dot{\theta}_2 = \dot{\phi}_1 = \dot{\phi}_2 = 0;$$

then

$${}_0\phi_2 = \frac{\omega \sin \lambda}{G\omega_2}\,; \quad {}_0\phi_1 = \frac{\omega \sin \lambda}{G\omega_1}\,;$$

$${}_0\theta_1(h\omega_1 + \omega \cos \lambda) = {}_0\theta_2 \,.\, h\omega_1 - n\omega_1\delta_0$$

$$= h\omega_1 \,.\, {}_0\theta_2 + \frac{\omega \sin \lambda \,.\, nd}{G\omega_2}\,;$$

and $${}_0\theta_2 = \frac{-2n \tan \lambda}{G}.$$

All these values are due to $\omega \sin \lambda$, and by putting a weight on the North side of the stable gyro and one on the South side of the unstable gyro, all can be reduced to zero as is done in the single-gyro compass.

Periodic Motion.

Let $\alpha = \alpha_0 + A\epsilon^{pt}$, $\beta = \beta_0 + B\epsilon^{pt}$, $\gamma = \gamma_0 + C\epsilon^{pt}$,
and $\delta = \delta_0 + D\epsilon^{pt}$.

A, B, C, and D are determined by the initial conditions and we have to eliminate these to determine the values of p. Substituting in equations (2) and eliminating A, B, C, and D, we get the determinant

$$\begin{vmatrix} p & 0 & -\frac{Gs}{2} & -\frac{Gd}{2} \\ 0 & p & -\frac{Gd}{2} & -\frac{Gs}{2} \\ \omega \cos \lambda & hs & p & nd \\ 0 & (hd + \omega \cos \lambda) & 0 & (p + ns) \end{vmatrix} = 0. \quad . \quad (3)$$

Expanding this we get

$$p^4 + p^3 ns + p^2 \,.\, Gs(hd + \omega \cos \lambda) + pnG\frac{s^2 - d^2}{2}(hd + \omega \cos \lambda)$$

$$+ \omega \cos \lambda(hd + \omega \cos \lambda) \,.\, G^2 \frac{s^2 - d^2}{4} = 0\,;$$

or

$$p^4 + p^3 ns + p^2 Gs(hd + \omega \cos \lambda) + 2pnG\omega_1\omega_2(hd + \omega \cos \lambda)$$

$$+ \omega \cos \lambda \,.\, hdG^2\omega_1\omega_2 = 0\,;$$

or if $\omega \cos \lambda$ is small compared with hd, we get

$$p^4 + p^3 ns + p^2 Gshd + 2pnGh\omega_1\omega_2 d$$

$$+ \omega \cos \lambda \,.\, hdG^2\omega_1\omega_2 = 0. \quad . \quad (4)$$

In order that the instrument may be a compass this equation must represent two damped oscillations, one being the oscillation of the two gyros together and the other their relative oscillation. The former is the period of the compass and the latter a much shorter period.

The first condition in order that this equation shall represent two damped oscillations is that all coefficients of p shall be positive *. That is satisfied if d is positive, *i. e.* if $\omega_1 > \omega_2$. That is, the stable gyro has smaller angular momentum (or greater gravity control) than the unstable one. The equation in p has to be resolved into two factors as follows :—

$$(p^2+2A_1p+A_1^2+B_1^2)(p^2+2A_2p+A_2^2+B_2^2) = 0,$$

in which A_1 and A_2 are the damping coefficients of the two oscillations, and B_1 and B_2 are the two frequencies or periodicities, *i. e.* $\frac{2\pi}{\text{period}}$.

When the damping is zero let p_1 and p_2 be the periodicities ; then

$$(p^2+p_1^2)(p^2+p_2^2) = 0 ;$$

or $$p^4+p^2(p_1^2+p_2^2)+p_1^2p_2^2 = 0.$$

If in equation (4) we make $n=0$, the damping disappears and

$$p_1^2+p_2^2 = Gshd, \quad p_1^2p_2^2 = \omega \cos\lambda \,.\, hdG^2\omega_1\omega_2 ;$$

and if $p_1 = 10p_2$ by assumption, then

$$p_1^2 \doteqdot Gshd,$$

and $$p_2^2 \doteqdot \frac{\omega \cos\lambda \,.\, G\omega_1\omega_2}{s}.$$

The second condition that equation (4) shall represent two damped oscillations is

$$p_1^2 > \frac{\text{coeff. of } p}{\text{coeff. of } p^3} > p_2^2,$$

or $$Gshd > 2Ghd \,.\, \frac{\omega_1\omega_2}{s} > \omega\cos\lambda \,.\, G\omega_1\omega_2\frac{1}{s} ;$$

or $$(\omega_1+\omega_2)^2 > \omega_1\omega_2, \quad \text{and} \quad 2h(\omega_1-\omega) > \omega\cos\lambda.$$

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* The conditions that an equation $p^4+ap^3+bp^2+cp+d=0$ shall represent two damped oscillations have been stated by Routh as (1) all coefficients must be positive and (2) $abc-c^2-a^2d>0$. This last condition leaves a very large range of choice of the coefficients, which must therefore be decided by other considerations.

The first is necessarily true and the second can be arranged by suitably choosing the torsion element.

The periodicity in the ordinary single-gyro compass is given by

$$p^2 = G\omega_1 \, . \, \omega \cos \lambda = \left(\frac{2\pi}{85 \text{ minutes}}\right)^2 .$$

Hence we see that if the gravity control of each gyro in the two-gyro compass is to be approximately the same as in the one-gyro compass—which must be the case if the ballistic deflexion is to take the compass on to the virtual meridian,—then the periodicity of the two-gyro compass must be less than that of the single-gyro compass in the ratio of $1 : \sqrt{2}$; *i.e.*, the period of the compass is increased in the ratio of $\sqrt{2} : 1$, or instead of being 85 minutes the period will be 120 minutes.

Assume arbitrarily the ratio $p_1 : p_2 = 10$, and also assume a ratio of $\omega_1 : \omega_2$ say 1·1 : that is, make the stable gyro with 0·9 of the angular momentum of the unstable gyro.

$$p_1^2 = 100\, p_2^2,$$

$$Gshd \doteq \frac{100\, G\omega_1\omega_2\omega \cos\lambda}{\omega_1 + \omega_2} ;$$

$$\text{or} \qquad h(\omega_1 - \omega_2) \doteq \frac{100\, \omega_1\omega_2}{(\omega_1 + \omega_2)^2}\, \omega \cos\lambda$$

$$\text{and} \qquad \omega_1 = 1{\cdot}1\, \omega_2 ;$$

$$\therefore \qquad h\omega_2 \doteq 250\, \omega \cos\lambda,$$

$$\text{or at } \lambda = 51^\circ \qquad h\omega_2 = \frac{2\pi}{9 \text{ minutes}}.$$

Hence a twist of 1 radian in the torsion element connecting the gyros would make the unstable gyro precess with a speed equal to one revolution in 9 minutes. This determines the stiffness of the torsion element.

It still remains to determine the stiffness of the suspension through which the damping torques are transmitted and to calculate the damping coefficients A_1 and A_2.

If we write equation (4) as

$$p^4 + ap^3 + bp^2 + cp + d' = 0,$$

the values of A_1 and A_2, the damping coefficients, are given by

$$A_1 \doteqdot \frac{a\left(p_1^2-\frac{c}{a}\right)}{2(p_1^2-p_2^2)} \quad \text{and} \quad A_2 \doteqdot \frac{a\left(\frac{c}{a}-p_2^2\right)}{2(p_1^2-p_2^2)}.$$

But

$$\frac{\frac{c}{a}}{p_1^2} = 2\,\frac{Ghd\omega_1\omega_2}{Gs^2hd} = \frac{2\omega_1\omega_2}{(\omega_1+\omega_2)^2} = \frac{2\times 1{\cdot}1}{(2{\cdot}1)^2} = \frac{1}{2}.$$

$$\therefore \quad A_1 = \frac{a(1-\frac{1}{2})}{2(1-\frac{1}{100})} = \frac{a}{3{\cdot}96}$$

$$\text{and} \quad A_2 = \frac{a(\frac{1}{2}-\frac{1}{100})}{2(1-\frac{1}{100})} = \frac{a}{4{\cdot}05}.$$

A_2 is the damping coefficient of the period of the compass. Suppose that we damp out the oscillation in one period, say, to 0·2 per cent., *i.e.* $\epsilon^{-2\pi}$; then $A_2 = \frac{2\pi}{120 \text{ minutes}}$ and $a = ns = \frac{2\pi}{30}$; $\therefore n\omega_2 = \frac{2\pi}{63 \text{ minutes}}$. Hence the twist in the suspension due to one radian difference of tilt will impart a precessional velocity to the unstable gyro equal to one revolution in 30 minutes.

$$A_1 = \frac{2\pi}{30\times 3{\cdot}96} = \frac{2\pi}{119 \text{ minutes}}.$$

Hence the short period is practically damped out in the same time as the long period.

It remains only to note that the torque in the suspension *assists* the precession of the unstable gyro when its tilt exceeds that of the stable one, otherwise it resists this precession. That is, if the North end of the unstable gyro is tilted above the North end of the stable one, the twist in the suspension forces the North end of the unstable gyro to the West.

The particular arrangement shown in figs. 1 and 2 has been selected because it makes the mathematical equations symmetrical for the two gyroscopes and introduces the minimum number of terms. The introduction of the viscous connexion between the gyroscopes adds more terms, as also does any other arrangement of the roller contact. This arrangement, however, serves to typify the mathematical methods.

In this connexion I would like to express my indebtedness to my mathematical colleague Professor Wm. Burnside, F.R.S., for valuable assistance in this and many other problems.

Summary.

The following is a summary of the results of the above discussion:—

It is shown how the two periods of oscillation of a structure carrying two gyroscopes such as a gyro-compass may be calculated; also the conditions for their mutual damping.

The undamped periods of the compass described are 120 and 12 minutes in latitude 51°.

Gravity control is such that $G\omega_1 = \frac{2\pi}{3\cdot14 \text{ minutes}}$: *i. e.*, if the gyro is tilted 30° from horizontal its axis will describe a cone round the vertical of 60° angle in $3\cdot14 \times \sqrt{3}$ minutes $= 5\cdot4$ minutes.

The unstable gyro has 10 per cent. greater angular momentum than the stable one.

The torsion element connecting the two gyros about the vertical is such that a twist of 1 radian would give to the unstable gyro a velocity of precession of 1 revolution in 9 minutes.

The suspension and the linkage to the switch producing the torque in the suspension are such that a tilt of one gyro through 1° relatively to the other produces a rate of precession of the unstable gyro of 0·64 degree per minute.

The long-period oscillation is damped to 0·2 per cent. in 120 minutes.

The short-period oscillation is damped to 0·2 per cent. in 120 minutes.

The compass settles on the meridian with both rotor axes horizontal provided that weights are placed on the N. end of the stable and S. end of the unstable gyros sufficient to produce the precession $\omega \sin \lambda$, the velocity of the meridian about the vertical.

XXX. *Dimensional Analysis.*

By NORMAN CAMPBELL, *Sc.D.*

[A reply to Mr. Buckingham's criticism (July 1924, p. 141) of my paper (March 1924, p. 481).]

I WAS careful to refrain from any direct criticism of Mr. Buckingham's work; but he has misinterpreted my meaning so gravely that I must be more definite.

I did not cast, and would never think of casting, the smallest doubt on the value of Rayleigh's use of the argument from similarity; and I share fully Mr. Buckingham's great admiration of the work of the Aeronautics Staff of the N.P.L., of which I was at one time an insignificant member. But I deny that this highly important work has anything to do with "dimensional analysis," as expounded by Mr. Buckingham and others. The question is not whether the argument is valuable, but what exactly the argument is.

Mr. Buckingham speaks of expounding the argument in text-book fashion. Alas, there are text-books and text-books! If a writer of a text-book on arithmetic devoted all his space to elaborate rules for drawing lines of the right width in the right places among figures entered in perfectly vertical columns, and if he omitted to point out that the operations entered in this beautiful manner must be conducted with an eye to the multiplication table, would he be able to rebut an accusation that the book was worthless by appealing to the great importance of arithmetic in technical physics?

The analogy is exact. The fundamental conception of the argument as used by Rayleigh is similarity. The concept of dimensions may be convenient in applying it; but Rayleigh did not always employ it, and, as I tried to show, it is never necessary. And yet in one of the papers which (I suppose) constitute the text-book * there is not a single mention of the word similarity, or of any synonym, and nothing but the most oblique hints that the systems to be compared must be even geometrically similar. There is no indication of why dimensions are relevant at all. The paper is a mass of elegant irrelevancies from which the one thing needful is carefully excluded.

The insistence on dimensions and the neglect of similarity is the direct cause of the errors to which I drew attention; nothing of physical importance can be derived from the consideration of dimensions alone. In fact, I would go further, and maintain that the conception of dimensions is totally useless and, in view of its dangers, should be abandoned. It was introduced originally to describe how the numerical value of a magnitude would change with the units employed in measuring it, on the assumption that the formal constants of the laws defining the magnitudes would always remain unaltered. Experience has shown that the assumption is untrue; physicists often find it convenient to change the formal constants rather than the numerical value. Moreover, units are now so standardized that the results of any change that ever occurs can be and are tabulated in detail; there is no need to consider how they can be deduced. The use of dimensions in checking an equation by examination of the dimensions of its two sides has also proved worthless; for equations which do not satisfy the criterion can be found in the writings of the most eminent physicists. Such discrepancies (usually due to the omission of "*c*") are doubtless due to inadvertence, and are not to be defended. But if the retention of dimensions in all our text-books cannot save us from such errors; if it encourages so greatly the activities of the modern equivalent of circle-squarers and leads to the abuse of one of the most valuable weapons of experimental research; is it worth while to puzzle with it the heads of our students and, incidentally, our own?

---

* E. Buckingham, Phil. Mag. xlii. p. 696 (1921).

XXXI. *The Cooling Power of a Stream of very Viscous Liquid.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a recent paper[*] I showed the effect of introducing a viscosity term into Boussinesq's treatment of the cooling power of a stream of inviscid fluid. In the analysis the equations of motion etc. were written down and certain substitutions were made for the variables involved. The resulting equations were quite free from terms representing the properties of the fluid etc. except that, in the notation adopted, a $c\,\nu/k$ group remained. It followed that the heat loss from similar bodies was given by

$$hL/k\theta = F[(v_\infty L/\nu);\ (c\nu/k)]. \quad . \quad . \quad . \quad (17)$$

This equation is true.

In the body of the paper it was indicated that for very viscous liquids the equation may tend to the form

$$hL/k\theta = F(v_\infty L/\nu).$$

---

[*] Phil. Mag. xliv. p. 940 (1922).

Unfortunately this is invalid, for it was erroneously supposed that if certain acceleration terms were neglected the $c\nu/k$ group would disappear from the equations. Actually, however, with the substitutions given, it remains as $(c\nu/k)\mathrm{T}'$.

For the amended analysis the correct substitutions can be obtained from those given in equation (5) by writing k/c for ν and $\mathrm{P}=\rho v_{\infty}^{2}(c\nu/k)\Pi$ for $\mathrm{P}=\rho v_{\infty}^{2}\Pi$. All properties of the fluid etc. then vanish from the transformed equations (6) and the boundary conditions (8), except that $(k/c\nu)(\mathrm{U}', \mathrm{V}', \mathrm{W}')$ occur in the equations of motion. From the heat flux relation it then follows generally that

$$h\mathrm{L}/k\theta=\mathrm{F}[(v_{\infty}\mathrm{L}c/k)\ ;\ (c\nu/k)],$$

an equation which is merely (17) in another form.

For very viscous liquids, however, $k/c\nu$ tends to be very small, and if the acceleration terms $(k/c\nu)(\mathrm{U}', \mathrm{V}', \mathrm{W}')$ are neglected we obtain

$$h\mathrm{L}/k\theta=\mathrm{F}(v_{\infty}\mathrm{L}c/k).$$

It is interesting that this simpler expression is of the same form as that which applies to inviscid fluids, the viscosity ν being absent. It is in good agreement with the tendency of my experiments on the forced cooling of wires*—for the most viscous liquids used the heat loss term tended to vary as $\mathrm{R}(v_{\infty}\mathrm{L}c/k)^{0\cdot 38}$, where the factor R represents certain residual effects.

I am, Gentlemen,
Yours faithfully,
A. H. DAVIS.

August 1924.

XXXII. *Notices respecting New Books.*

The Measurement of Fluid Pressure and Velocity. By J. R. PANNELL. (Arnold & Co. 10*s.* 6*d.*)

THIS volume, which is a notable production of the Aerodynamics Department of the National Physical Laboratory, has a sad history. It is edited by Mr. Frazer, of the Department, and opens with a foreword by Mr. Southwell, the head of the Department. Mr. Pannell was killed in the trial flight of the rigid airship R. 38, after notable work on the speed and general properties of the airship. His notebooks were partially rescued from the wreck, and showed that this work, on his part, had continued almost to the moment of the disaster. He was one of the original members of the Department.

Mr. Frazer has completed a manuscript which he left as the foundation of a treatise on fluid pressures and velocities. To a great extent, we must regard this as a memorial volume. The various subjects discussed comprise pressure-tube instruments, of which a very complete account is contained in the first chapter; various anemometers, to which the second chapter is devoted, and which may in general be described as moving-part anemometers; hot wire anemometers; direction and velocity meters, and manometers. The work is unique in the comprehensive and balanced account which it gives of all these instruments, none of which, in a modern form, finds a place in any text-book. A final chapter examines the flow of fluids in circular pipes, and is rather more theoretical.

---

* Phil. Mag. xlvii. p. 1057 (1924). The empirical formula given in the summary tends to the form stated, since m and n tend respectively to 0·19 and 0·38.

We cannot describe the proof-reading as having been entirely satisfactory. For example, it is somewhat of a shock to see Euler referred to on p. 51 as "Eulzer," in relation to a notable constant which he introduced. Such blemishes are too numerous, and perhaps may disappear in a new edition, which, in a country becoming more alert to the practical side of aerodynamics, will no doubt be called for. The fundamental value of the work lies on the side of the practical description of instruments.

On the direct numerical Calculation of Elliptic Functions and Integrals. By Prof. L. V. King. (Camb. Univ. Press, 3*s*. 6*d*. net.)

This little work really does fulfil a long-felt want. It is dedicated to the memory of the late Prof. Harkness, of McGill University.

In spite of all the efforts of, for example, Sir George Greenhill, the numerical tabulation of elliptic functions has not advanced much beyond the point where Legendre left it. It is an expensive matter, and funds do not seem available. It is too customary for the mathematician to regard a problem as solved when its answer is expressed in a standard form of elliptic integrals. The physicist, confronted with this, merely gasps, and proceeds to find an alternative solution in his laboratory. Prof. King, who belongs to both categories, refuses to be satisfied with this position, and he explains, in his preface, just how he was led to the present work by the need for accurate values of the coefficients of self- and mutual-induction of coils.

He makes no claim to novelty in formulæ or in methods of computation, but, nevertheless, we find a great deal; and the work is in fact a notable contribution towards the simplification of the necessary calculations. We can only regret that it perforce stops short with the demonstrations of the proper mode of calculating the Tables in a numerical way. Physicists need tables of elliptic functions on a scale commensurate even with tables of logarithms.

Collected Researches from the National Physical Laboratory. Vol. xvii. 1922. (H.M. Stationery Office. 17*s*. 6*d*. net.)

This volume follows the usual lines of the series issued by the National Physical Laboratory. All the papers included have, of course, already been published elsewhere, and the value of the work lies in the fact that it gives an epitome of the published papers of the Staff of the Laboratory ranging over a given time. They are restricted entirely to optical work and its various side-issues, and are taken from the Proceedings of the Physical Society, the Optical Society, and the Philosophical Magazine. The output is very large, and contains notable contributions to the detail of the subject, and more especially to its application. What is usually called "geometrical optics" is in question, and it is to some extent a matter of regret that so little attention is given in the laboratory to the fact that rays of light have wave-properties, so that the more striking refinements of optical methods recently worked out elsewhere depend so much on the phenomena of interference and of diffraction of light. We cannot avoid the feeling that there is some scope in a Department of this type for a broader outlook on optical questions, in so far as future development of accurate method is intended. But we can only congratulate the various authors on the meticulous care which they take to explore every detail which the older methods still lack, in regard to precision of statement and of inference.

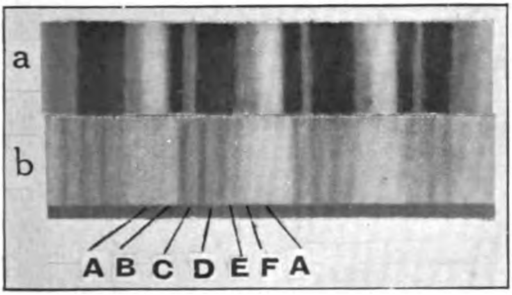
Applied Elasticity. By J. Prescott. (Longmans, Green & Co. 25*s.* net.)

This is a work which we can recommend, with some confidence, to the engineer or physicist whose mathematical equipment is not too limited. The author, while stating that the work contains little which can not be found in mathematical treatises on the theory of elasticity, expresses his intention of writing a book for the practical engineer. He follows this object by severe limitation of his illustrative examples to those which can lead to the solution of practical problems. In this respect we consider that his choice is, on the whole, excellent. He leaves aside certain matters on which theory and experiment are not quite in line, and confines himself to the matters on which there is no doubt. A practical man who can read the book will certainly trust it, for he will not find anything of importance which seems to contradict his experience.

Approximate methods of solution based on the principle of minimum energy are used to an unusual extent, for a sufficiently valid reason which the author explains, and a reason which, however unsatisfactory to the logical sense, is certainly, in its results, effective in practice. He thus avoids much tedious analysis on important problems, especially those relating to questions of stability, and of normal elastic oscillations. The book contains also a certain amount of original matter due to the author, and not hitherto published.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

I.



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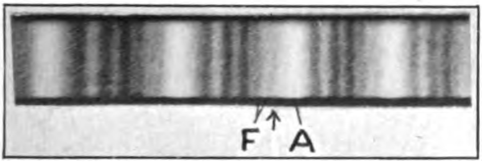

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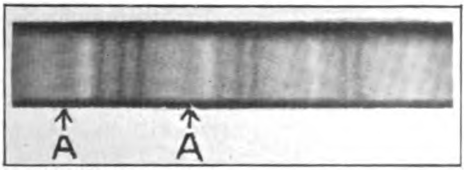

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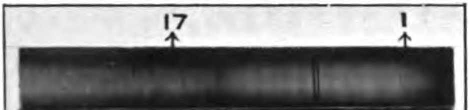
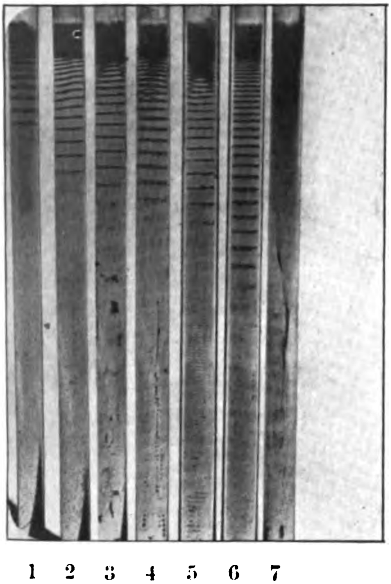


Fig. 3.

Scott Blair. Phil. Mag. Ser. 6, Vol. 49, Pl. III.



Ages.

Tube.	Age.
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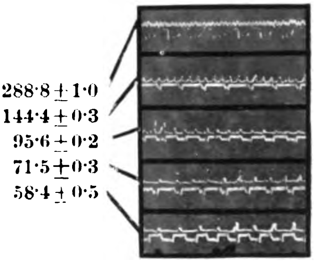
7	13 days.

Fig. 1.



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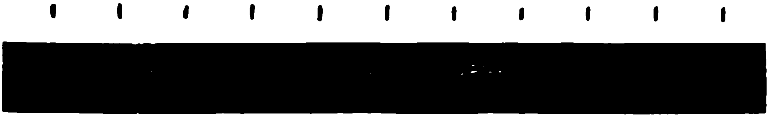

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SIXTH SERIES.

N° 290.—FEBRUARY 1925.

WITH THREE PLATES.

Illustrative of Mr. C. E. WYNN-WILLIAMS's Paper on a Piezo-Electric Oscillograph; Mr. U. DOI's on a New Discussion of Bucherer's Experiment; and Mr. G. E. BELL's on the Impact with Liquid Surfaces of Solid Bodies of Various Shapes.

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[SIXTH SERIES.]

FEBRUARY 1925.

XXXIII. *A Piezo-Electric Oscillograph.* By C. E. WYNN-WILLIAMS, *M.Sc.*, *University Research Student, University College of North Wales, Bangor* *.

[Plate V.]

THE present research was undertaken with the object of ascertaining whether a practical oscillograph could be constructed by utilizing what is known as the converse piezo-electrical effect, and if so, of examining its characteristics.

The converse piezo-electrical phenomenon consists of the mechanical strain produced in a crystal when suitably electrified. This strain may be a linear extension or contraction, as in the case of quartz, or a combined linear and torsional effect as in the case of rochelle salt crystals.

It was thought probable that an oscillograph constructed on this principle would possess certain advantages over some of the types at present in use. In the first place, it would probably have a small capacity, and, being electrostatic, would not interfere to any great extent with the working of the apparatus to which it was connected. As most electrostatic oscillographs at present in use require high voltages to obtain appreciable amplitudes, it was thought that by suitable choice of material an advantage would be gained by being able to operate at a comparatively low voltage. In addition, as the present low-voltage oscillographs are mostly current operated, and not electrostatic, the advantages of both types would be combined in one instrument. A further possibility lay in the fact that the natural frequency of vibration of a crystal might be high, a desirable feature in all oscillographs.

---

* Communicated by Prof. E. Taylor Jones, D.Sc., F.Inst.P.

The piezo-electric substances experimented with in the present research are quartz and rochelle salt. Other substances, however, show this effect, *i. e.* boracite, tourmaline, etc. In a paper by Dr. Nicolson[*], it is stated that most substances which exhibit optical activity also show this phenomenon. He points out that it is probably due to asymmetry in the crystal,—molecular in the case of quartz, boracite, etc., and atomic in the case of organic substances like rochelle salt. He states that up to the time of writing rochelle salt has been found to have the greatest known activity, but it is quite probable that other substances may be discovered possessing a greater sensitivity. Dr. Nicolson also shows that, by special treatment, the sensitivity of rochelle salt may be increased, and that under suitable conditions of growth, crystals are obtained which show a torsional effect not present in the normal crystal.

It was hoped that amongst the substances which show this effect, one or more might be found to be suitable for the purpose of oscillograph construction. In order to see what condition the substance should, however, fulfil, it will be well to examine the theory of the oscillograph in a general way.

Theory of the Oscillograph.

In principle the oscillograph is an instrument which gives a graphical representation of some varying quantity such as an electrical current or potential. This is done by making the electrical quantity control the movement in one direction of a spot of light falling on a photographic plate or film. Either the plate or spot is also moved at some definite rate perpendicularly to this direction, the plane of the plate being at right angles to both of these directions. In this way the light spot describes a curve relatively to the plate, which curve is photographed. From this, provided the characteristics of the instrument are known, the value at any moment of the quantity under consideration can be calculated. If possible it is arranged that the spot moves with uniform velocity along the "x" axis of the plate, the "y" coordinate being a function of the electrical quantity under examination, so that x is proportional to the time, while y is usually proportional to the electrical quantity E, or to its square. If y is a linear function of the electrical quantity, a scale representation of it results.

---

[*] A. M. Nicolson, "The Piezo-Electric Effect in the Composite Rochelle Salt Crystal," presented at a joint meeting of the A.I.E.E. and the American Physical Society, Philadelphia, Pa., Oct. 9, 1919.

The nearest approach to the ideal instrument is the cathode ray oscillograph, in which the mechanical-electrical medium is a beam of cathode rays deflected by an electrostatic or a magnetic field. Here the inertia of the system is negligible. In practically all other oscillographs the position of the spot is determined by a mirror, which, in turn, is controlled by the electrical quantity. This introduces extra inertia, which distorts the curve obtained, and limits the usefulness of the instrument.

If the system has a natural periodicity n, and specific damping k, and is not a coupled system, we get for the dynamical equation,

$$\frac{d^2y}{dt^2} + k\frac{dy}{dt} + n^2y = \mathrm{E},$$

where E represents the applied force per unit of inertia. Here it is assumed that a linear relation exists between the displacement and the applied force, and that n and k are constants. Expanding E by Fourier's theorem we get

$$\mathrm{E} = \mathrm{E}_0 + \sum_{m=1}^{m=\infty} \mathrm{E}_m \epsilon^{-\mu_m t} \left\{ \begin{matrix} \sin \\ \cos \end{matrix} \right\} mpt.$$

Substituting this expression for E in the differential equation and integrating, we get

$$y = \mathrm{A}\epsilon^{-\frac{k}{2}t} \sin\left(\sqrt{n^2 - \frac{k^2}{4}}\, t + \alpha\right)$$
$$+ \left[\frac{\mathrm{E}_0}{n^2} + \Sigma \frac{\mathrm{E}_m \epsilon^{-\mu t} \left\{ \begin{matrix} \sin \\ \cos \end{matrix} \right\} (mpt - \phi)}{\sqrt{\{n^2 - m^2p^2 + \mu(\mu - k)\}^2 + m^2p^2(2\mu - k)^2}}\right]$$

where $$\tan\phi = \frac{mp(k - 2\mu)}{n^2 - m^2p^2 + \mu(\mu - k)},$$

The first term of the expression (*i. e.* the complementary function) represents the free oscillations of the system in its own period. It will be observed that these die away unless $k = 0$. If k is not less than $2n$, no free oscillations will be recorded, the system being aperiodic. As it is undesirable to have the free oscillations recorded, it is arranged that k shall not be less than $2n$. This is the first requirement.

The second part of the solution—(the particular integral)—represents the forced oscillations of the system produced by the electrical force. Every term in the expression for E has a corresponding term in the solution, so that all harmonics appear in the record. It will be observed, however, that although the periodicity, p, and the damping, μ, are correctly recorded, the amplitude scale and the phase lag, ϕ, are functions of p, and are therefore different for the various components of E, consequently the curve is usually distorted to some extent, and does not give a true representation of the quantity E.

To examine this distortion, assume that E is a harmonic function without damping; then the second expression reduces to

$$\frac{E\sin(pt-\phi)}{\sqrt{(n^2-p^2)^2+k^2p^2}},$$

where $\tan\phi = \dfrac{kp}{n^2-p^2}$.

The amplitude scale is given by

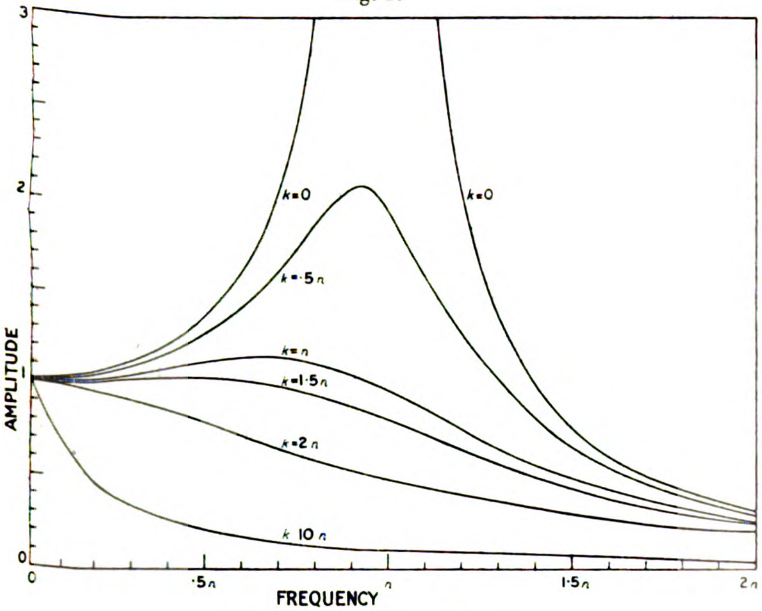
$$\frac{E}{\sqrt{(n^2-p^2)^2+k^2p^2}},$$

and is shown plotted against p for various values of k in fig. 1. When $k=0$, we get the ordinary resonance curve, with an infinite amplitude at $p=n$. As it is desirable to have all oscillations recorded with the same amplitude scale, the curve for $k=1{\cdot}5n$ would seem to be a suitable one, as it is fairly flat for some distance from the origin, but since k must not be less than $2n$ to ensure aperiodicity, the instrument will have to be worked on the curve for $k=2n$. In this case the amplitude of the oscillations decreases as the frequency increases. Although this may be corrected for, it is usual to keep the working range small, say from $p=0$ to $p=0{\cdot}1n$ or $0{\cdot}2n$, and to ignore the error (*i. e.*, the error introduced by assuming that the amplitude is constant and equal to its value at $p=0$). In the first case this amounts to 0·7 per cent., and in the latter, 4 per cent. for this curve.

Thus, in order to obtain a true record, the natural frequency of the instrument must be from five to ten times greater than the highest frequency to be recorded, when dealing with more than one oscillation. This gives the second condition to be fulfilled.

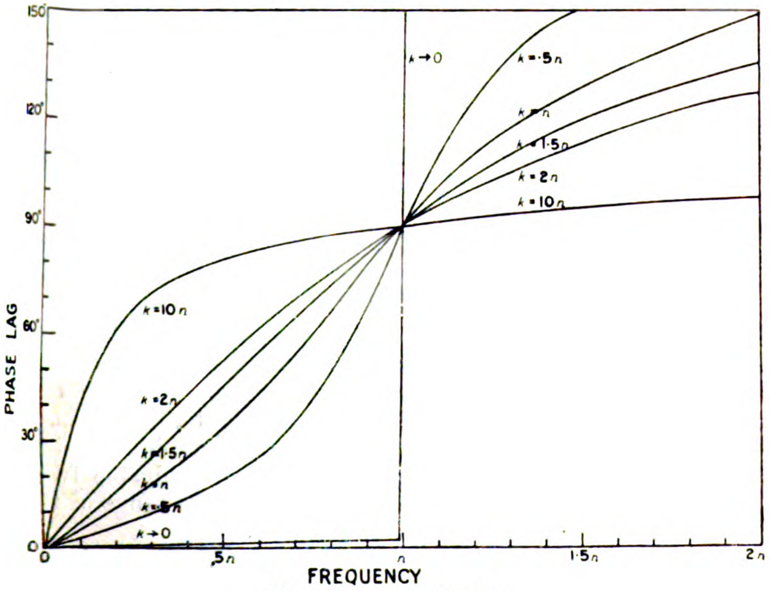
The variation in phase lag is shown in fig. 2, ϕ being plotted against p for various values of k. It will be seen

Fig. 1.



Amplitude-frequency Curves.

Fig. 2.



Phase-frequency Curves.

that for $k=2n$ the curve is fairly straight over the ranges $p=0$ to $p=0{\cdot}1n$ or to $p=0{\cdot}2n$, the respective errors introduced by assuming a constant phase lag being about 3 per cent. and 7 per cent. This again emphasizes the fact that the natural frequency of the instrument must be high.

Summing up, we see that the requirements of an oscillograph are :—

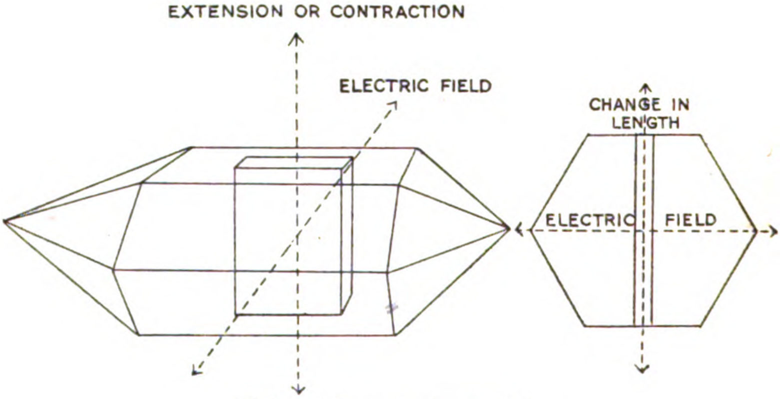
(1) The mechanical system must have as high a natural frequency as possible, at least 5–10 times that of the highest frequency to be recorded, or distortion will result.

(2) The system should be made aperiodic.

(3) It is *convenient*, but not essential, that the relation between the displacement and the applied force should be linear.

The last two conditions are fairly easy to satisfy, but the first presents some difficulty when it is desired to record high frequency oscillations. The highest frequency obtainable in most "strip" oscillographs (such as the Duddell) is of the order of 10,000 per second, so that the limit of working is about 1000–2000 vibrations per second. It is in this connexion that piezo-electricity is resorted to, in the hope that the natural frequency of some of the piezo-electric crystals may be so much higher than that obtainable from the present mechanical systems as to enable the range of the oscillograph to be substantially increased.

Fig. 3.



Slab cut from quartz crystal.

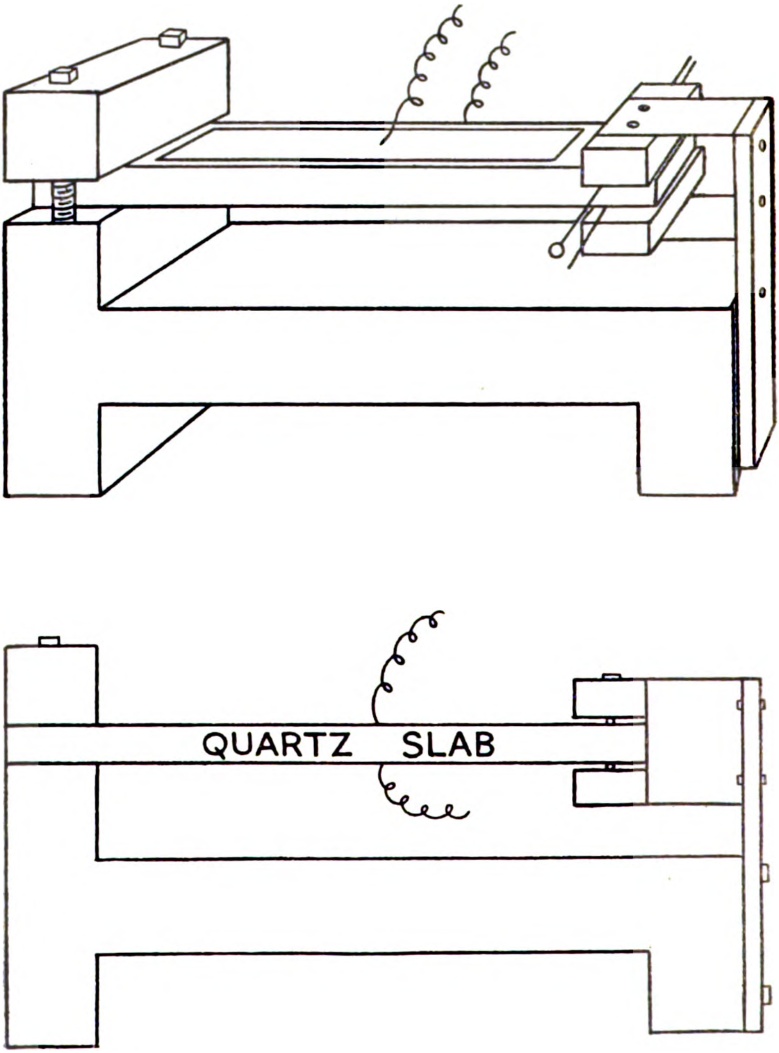
Suppose that a strip of quartz is taken. The velocity of sound in quartz is about 400,000 cm./second. If the strip is 5 cm. long and has one end clamped, the free end can execute a longitudinal vibration of frequency 20,000 per second. By cutting the slab of quartz from a crystal in the manner shown in fig. 3, so that the long edge is 5 cm. long, and clamping it at one end, the faces of the slab being silvered and connected to a source of alternating E.M.F., the free end will execute forced oscillations of the same frequency as the source. Hence, provided the movement can be recorded, an oscillograph of high natural frequency is obtained. The first experiments in the present research were undertaken with the object of ascertaining whether the movement was large enough to be recorded and so be turned into practical use.

Experiments with Quartz.

A slab of quartz, suitably cut, was obtained, of dimensions 5 cm. × 2 cm. × 0·3 cm. This was carefully silvered and copper plated. The copper was then removed round the edges, until only two plates were left on the faces, with about 1 mm. clearance along the sides, and about 5 mm. at the ends. Leads were connected to both plates. One end of the slab was firmly clamped. The other end was covered with thin emery paper to give a frictional surface, and two thin steel needles, 0·7 mm. diameter, were held against the emery paper by two ebonite blocks (also covered with emery paper) fastened to the end of a V-shaped spring. This in turn was clamped to the base. A small mirror was fastened to the end of one of the needles. Fig. 4 shows a section and sketch of the instrument. Any change in length of the quartz would thus produce a rotation of the needles and so tilt the mirror. A spot of light, reflected from the mirror, was carefully watched while the plates were raised to a P.D. of about 10,000 volts (direct), but no movement was observed. This was the highest voltage that could be reached in air, so the whole instrument was immersed in oil and the experiment repeated, with no better results.

It was thought that interference methods might give better results; various methods were experimented with, the most satisfactory being the "Newton's rings" method. A small piece of blackened glass was attached to the free end of the quartz, and a long-focus lens to the base of the instrument, parallel and close to the glass. Rings were seen, using a sodium flame as a source of light. These were observed through a telescope, while the plates were charged to about

Fig. 4.



Quartz Oscillograph.

10,000 volts by means of a small wimshurst machine. It was found that about 10,000 volts (measured by the spark length) would produce a movement of one ring (from "dark" to "dark"). Hence the free end must have moved through a distance equal to half the wave-length of sodium light, viz.:—$2{\cdot}948 \times 10^{-5}$ cm. This movement was smaller than was expected, and accounts for the fact that no measurable deflexions were obtained by the mirror method.

It was decided to abandon the quartz (temporarily at least) and to turn to rochelle salt, which is much more sensitive, as an alternative.

In passing, it is interesting to note that audible "clicks" were heard from the quartz on charging and discharging the plates from the 200 volt mains. Assuming a linear voltage-displacement relation, it will be seen that the movement of the free end is only $5{\cdot}897 \times 10^{-7}$ cm. Later, on trying the effect of alternating E.M.F.'s of about 150–200 volts (R.M.S.) supplied by a valve, audible notes were produced. This method could evidently be used for the determination of the minimum intensity of sound necessary for audibility.

Rochelle Salt.

Crystals of rochelle salt are much more sensitive than quartz. The piezo-electric properties of this substance have been made the subject of considerable research during the last three or four years, especially in America. Valasek * has shown that the substance exhibits a kind of hysteresis similar to magnetic hysteresis, and has succeeded in obtaining a loop for it, of a similar shape to a magnetic hysteresis loop.

Dr. Nicolson, of the Western Electric Company, has shown that with suitable conditions of growth, a crystal may be obtained which will exhibit a torsional piezo-electrical effect. Ordinarily the crystals are of the shape shown in fig. 5 A. Such crystals are formed by growing on a mercury surface, or by being suspended in the solution. If a slice be cut from such a crystal, normal to the (*a*) axis, and having edges making angles of 45° with the (*b*) and (*c*) axes, the slice will exhibit piezo-electrical phenomena similar to quartz. This effect is purely linear. If, however, a crystal is grown on a piece of plate glass or mercury surface, with the (*a*) axis vertical, a sort of "flat" crystal is obtained. (See fig. 5 B. Figs. 5 A and 5 B are reproduced from Nicolson's paper.) Crystals so grown, especially those grown by cooling a saturated solution, show a peculiar marking, termed an "hour-glass" marking. The small crystal used as a nucleus lies in the centre of the flat face, and as the crystal gradually grows, different layers become strained, giving the peculiar appearance [*] shown in fig. 5 c. It will be observed that the crystal appears to contain two pyramids, having their apices on the nucleus, and their bases at the ends of the crystal. If these two pyramids are connected to one terminal of the voltage supply, and a connexion from the other terminal is made to the rest of the crystal, so that both pyramids are charged with respect to it, an internal torsional stress is set up, which results in the top pyramid being twisted relatively to the bottom one about the (*c*) axis. The magnitude of this twist depends upon the particular crystal, and may be large or small, regardless of size of the crystal, dryness having much influence. In Nicolson's paper it is mentioned that soaking the crystal in alcohol for some hours

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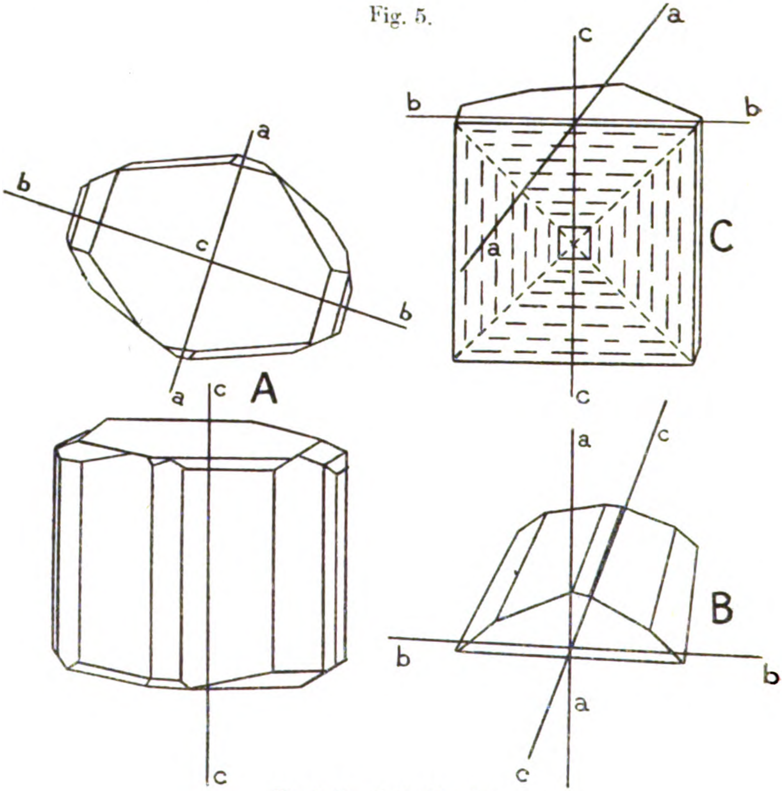
* Valasek, "Piezo-Electric and Allied Phenomena in Rochelle Salt," Phys. Rev. April 1921.

Fig. 5.



Rochelle Salt Crystals.

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[*] Such crystals are termed "composite."

before drying increases this effect, and that only crystals showing the hour-glass marking give rise to large values. He states that in one case (a crystal 7 cm. long) a twist of 10^{-5} radian per volt was obtained.

In practice, connexion is made to the crystal by two tinfoil electrodes fastened to the ends (by wax or shellac varnish) and by a third "girdle" of foil round the middle of the crystal. The width of this latter is usually about one-half to three-quarters the length of the crystal. The two ends, connected together, form one pole, and the girdle the other. Wood's alloy has also been used for the end electrodes.

Evidently the electrical conditions within the crystal are much more complex than within a "plate." As far as can be ascertained, the theory has not yet been worked out for this type of strain.

A torsional strain being much more easily magnified, it was decided that this type of crystal might be used more successfully for oscillograph purposes than quartz, as it has also the advantage of being more sensitive, and therefore of requiring a lower working voltage.

Growth of Rochelle Salt Crystals.

Several experimenters engaged in research on this substance, and also some chemical firms, were communicated with to see if the finished crystals could be obtained, but unfortunately none were available *. Accordingly much time had to be spent in growing suitable specimens.

The only available information on this subject was obtained from Nicolson's paper. As, however, only a general outline is given by him, and no details are furnished, a number of different conditions of growth had to be tried.

In the first experiments, growth was attempted by the slow evaporation of a solution of the salt, at room temperature. Small fairly well shaped crystals were obtained in this manner, but they were perfectly clear, and did not show the composite structure mentioned, which appears to be necessary for the torsional effect. The effect of hastening the rate of evaporation was tried by placing the containing vessel on a board over a gas radiator. This resulted in the crystals forming more quickly, but trouble was caused by small crystals formed at the surface of the liquid falling on top of the "seed" crystals at the bottom of the vessel, and so disturbing the growth.

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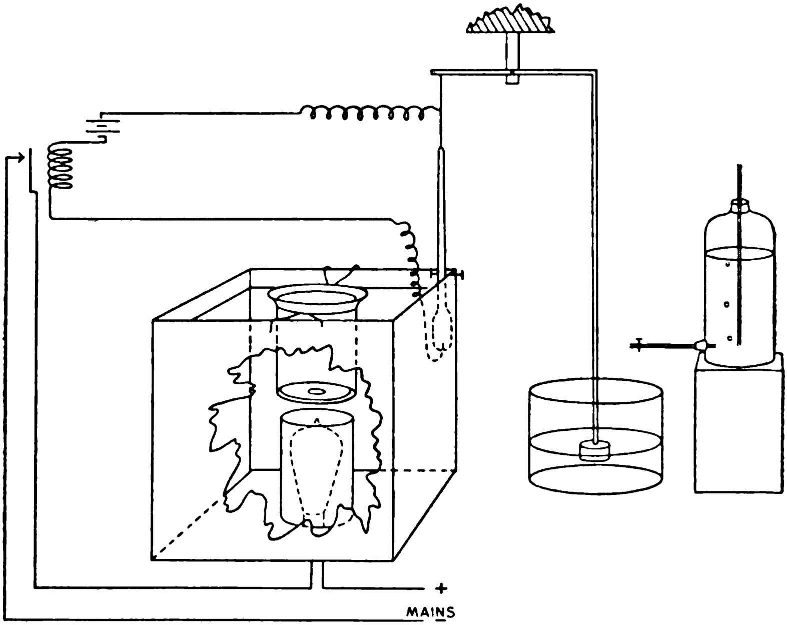
* Since the above was written, a large specimen has very kindly been presented by the International Western Electric Co., to whom the writer's thanks are due. So far, no opportunity has been found for testing it, but in appearance it resembles those obtained by the writer.

Experiments were then conducted to see if crystals could be obtained more readily by cooling a saturated solution. A saturated solution contained in a beaker was placed in a larger vessel full of water at the same temperature (about 30° C.). This latter vessel was jacketted with cotton-wool. A small seed crystal was introduced into the saturated solution, and the whole left to cool overnight. This method resulted in a crop of small irregular crystals—evidently due to too rapid a fall of temperature. This was repeated with the whole apparatus placed over a radiator, whose temperature was slowly lowered by periodically turning the gas lower. The resulting crystals were a little better, but not satisfactory; evidently uneven heating was one source of trouble.

Fig. 6.



Thermostat and Control.

A method which gave good results was found by constructing a thermostat whose temperature could be automatically lowered at any desired rate. Fig. 6 illustrates the arrangement. The water-bath consisted of a cubical tin box of about 9 in. side. Into the bottom of this a cylinder was let, open from the outside, in which an electric lamp could be placed to supply the necessary heat. A 60 watt lamp was found to be ample to keep the bath at 50° C. The box was jacketted with cotton-wool. A thermometer was constructed from fairly wide capillary tubing, with a platinum contact fused into the bulb. This was placed in the bath. A wire passed down the bore of the tube to make contact with the mercury thread at any desired temperature. When contact was made, a local low voltage circuit was closed, which resulted in the lamp being extinguished by means of a reversed relay. The thermometer contact was sensitive to about 0·3 of a degree. In order to lower the temperature automatically, the upper end of the wire was attached by means of a lever to a float in a vessel of water. Water dropping from a capillary tube connected with a constant-pressure bottle slowly raised the float and so pushed the wire down the thermometer. By this means, the temperature could be lowered as slowly as 0·5 degree per hour.

The actual growth took place in a beaker of about 700 c.c. capacity suspended in the bath. As these crystals require to be grown on a flat surface, a layer of mercury was placed at the bottom of the beaker. It was found, however, that as the crystal increased in mass it sank a little further into the mercury, and so developed a slightly convex surface. This was rectified by growing the crystals on a piece of plate glass floating on the mercury. This ensured that the surface was both level and flat.

Seed crystals were obtained by cooling rapidly, and from the crop of small crystals so obtained, suitable ones were picked out.

The solution must be carefully filtered, otherwise dust, etc., form nuclei for crystals. The best method of carrying out this method was found to be as follows. The saturation temperature of the solution was determined previously, and the thermostat brought to about 3 or 4 degrees above this temperature. The solution was heated to the temperature of the thermostat, and the seed crystal warmed to this temperature by being placed for a few minutes in a dry test-tube immersed in the solution. Unless this was done, the crystal cracked on being dropped into the solution, on account of the sudden expansion of the outer layers. The beaker containing the solution was then suspended in the thermostat, the glass plate and mercury dropped in, and, finally, the seed crystal was introduced and moved to a suitable position near the centre of the plate. It was found necessary to suspend a sort of "umbrella" consisting of a circular glass plate, slightly less in diameter than the beaker, just below the liquid surface. This prevented crystals formed at the liquid surface from falling on the growing crystal and hindering perfect formation.

It was found best not to cool continually, but to lower the temperature slowly (about 1° per hour) to about 2 or 3 degrees below saturation temperature, and to keep the solution at this temperature for some time. With care, crystals as large as 6 cm. × 5 cm. were grown by this method.

The actual time of growth varied with the size of the crystal. A crystal 2 cm. × 2 cm. could be grown in about 8 hours. It was found difficult to prevent the larger crystals from developing flaws due to side growths.

Another method that gave good crystals was to allow a solution to cool in a small hot-air oven. This consisted of a cubical copper oven, about 1 ft. side, covered with cotton-wool, and heated by means of a 20 watt electric lamp placed inside. Provided it was left undisturbed, in a room free from draughts, the temperature was found to keep constant to within about 1° C. for long periods,—about 12 hours or more,—without the use of a regulator.

A solution, saturated at about 3 or 4 degrees above the oven temperature, was heated to about 8 degrees above that temperature, and the seed crystal introduced as before, together with the plate, mercury, etc. The whole was then left in the oven for about 12 hours. Crystals up to about 4 cm. square were obtained by this method.

The latter method seemed to yield the better formed specimens, and it was more free from trouble due to small crystals interfering with the growth than any of the other methods tried. Probably the solution was kept at a more uniform temperature throughout than it was in the thermostat method, in which no stirring apparatus was provided.

Crystals of all sizes from about 1·5 cm. square to about 6 cm. were grown and tried. It was exceedingly difficult to prevent the large crystals from developing flaws and cracks. They often cracked, on being removed from the solution, in coming into contact with cold air, even the temperature of the finger being sufficient in some cases. On the whole, crystals 2–4 cm. square were the largest which could be grown satisfactorily.

Preparation of the Crystals for Experimental Work.

According to Nicolson, if the crystals are soaked for some hours in alcohol, and dried, they are rendered more sensitive for the direct piezo-electric effect. This has been found to be the case for the converse effect also, and for oscillograph work an additional advantage arises from the fact that crystals so treated appear to stand the voltage better than the raw crystal. So far, it has not been ascertained whether the treatment affects the natural frequency and damping of the crystal, but it is quite possible that these properties are affected by the degree of dryness of the crystal.

While Nicolson finds desiccation of the crystal to be an advantage, Valasek shows that the linear piezo-electric effect is decreased by drying. It should be mentioned, however, that Valasek carried his drying process to a higher stage than Nicolson by using phosphorus pentoxide. This may possibly account for the different results obtained by the two experimenters.

On the whole, for the purpose of the present research, it has been found advisable to soak the crystal in alcohol, even if only on account of the increase in dielectric strength.

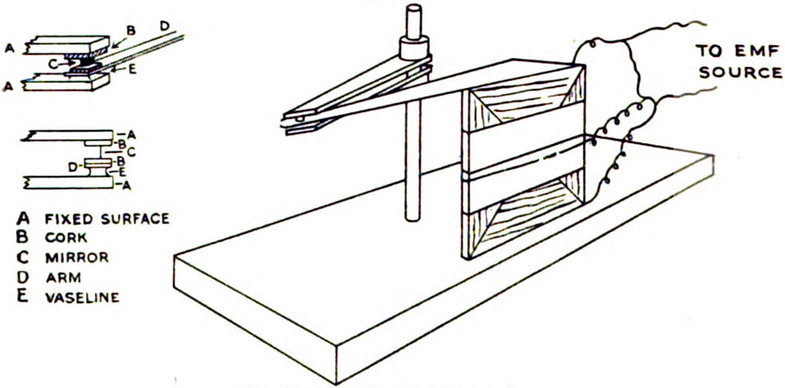
The crystal is taken from the solution and immediately placed in a vessel full of alcohol, at the same temperature as the solution. It is at this stage that cracks usually appear, and care must be taken not to let the crystal experience any sudden change of temperature. It is left in the alcohol for about 12 hours, preferably in a warm place, and then a fresh supply is poured on for a further six hours. This treatment changes the appearance of the crystal somewhat, the clearness disappearing and being replaced by a translucence. After the soaking has been completed, the crystal is removed and placed in a drying oven, kept at a temperature of from 35° to 40° C., for several days—the longer the better. 40° should not be exceeded as the crystals lose their sensitiveness if heated too strongly.

The electrodes consist of pieces of tinfoil cut to appropriate shapes, tags being left on for connexion. Low melting wax (below 40°) or shellac varnish may be used to attach them to the crystal. The latter is the more satisfactory, but the crystal must be re-dried after application. The width of the girdle should be about one-half the length of the crystal, and the electrodes should be well pressed into position, a thin coating of shellac varnish having been applied previously. Celluloid dissolved in amyl acetate has also been used for this purpose; it has the advantage of setting more quickly than shellac. Wood's metal is not recommended for two reasons. In the first place, 55° C., its melting point, is rather too high a temperature to which to subject the crystal, and also, the large masses at the ends would tend to lower the natural frequency. The melting point can be lowered by the addition of mercury, but on the whole this material is not satisfactory. Filing the ends of the crystal concave, as recommended by Nicolson, was not found to cause any improvement. Very often this process causes flaws to appear. The crystals were used in the form which they had when taken out of the solution, and were found to possess sufficient sensitiveness in this form after treatment with alcohol.

Preliminary Measurements.

Measurements made with a crystal 2·5 cm. square by 1 cm. thick showed that the torsion was proportional to the voltage, and for 200 volts was about 10^{-4} radian. A dissymmetry for + and − potentials was also observed, the deflexions being greater in one direction.

Fig. 7.



Rochelle Salt Oscillograph.

In order to obtain sufficient magnification, a light but rigid arm of sheet aluminium, folded so as to have a girder section, was attached to the top of the crystal, extending horizontally to 2 or 3 cm. from the centre of the crystal. Between this arm and a fixed surface placed just above it was held a small plane mirror, about 1 square mm. in area. The plane of the mirror was parallel to the plane face of the crystal. When too thin and clamped in this way, the mirror was liable to be bent slightly convex or concave, making sharp focussing of the spot impossible. Accordingly thicker mirrors had to be used. In order to prevent slipping, the tip of the arm and the fixed surface were covered with thin slips of cork. This arrangement was found to be very satisfactory, amplitudes of 1·5 cm. on either side of zero being at times obtainable, using an image distance of 1 metre. Fig. 7 shows the arrangement.

The actual arrangement of the apparatus for recording the curves is as follows:—The whole is set up in a darkened room. A small pinhole, having the crater of an arc lamp focussed on it, is used as a source of light. From this, a beam falls on the oscillograph mirror, and (if required) on to a mirror attached to the prong of a tuning-fork placed near the oscillograph. This gives a time scale if the frequency of the fork is known. These mirrors are so arranged that on tilting they deflect the beam in a vertical plane. After reflexion from the small mirrors, the beams fall on a concave mirror, of about 50 cm. radius of curvature, attached to a horizontal turntable, rotated at any desired speed by an electric motor.

It is desirable (for reasons to be given later) that the crystal should not be subjected to the E.M.F. longer than is necessary, so a cam was arranged on the turntable which opened and closed a two-way mercury switch, at the moment when the spot of light passed the plate. Normally, the crystal was shortcircuited by one contact. At the correct moment this was broken, and contact was established with the live cup. This was also found useful for "make" and "break" photographs, etc. A safety resistance was placed in the circuit, consisting of a 200-volt metal filament lamp, to prevent inconvenience due to shortcircuit. (The impedance of the crystal was large compared with the resistance of the lamp.)

In order to determine whether the crystal was suitable for oscillograph work, investigations were conducted to determine whether the ncessary conditions were satisfied. In the first place it is necessary to know what relation exists between the applied E.M.F. and the corresponding displacement. Rough measurements had already been made as to the deflexions at various voltages, and, as far as could be judged, a linear relation seemed to exist. It must be observed, however, that equal + and − voltages do not necessarily or generally give equal + and − deflexions,—*i.e.*, the voltage-deflexion curve is not the same on opposite sides of zero. The effect of this on an oscillogram is to make one side of the curve appear to have a greater amplitude than the other —a sort of rectification effect such as is obtained in wireless by working at the lower bend of a valve characteristic. This is not serious unless the change of the voltage-deflexion curve is very pronounced. As a rule, it may be neglected, as there is practically no distortion. It is possible, however, to overcome the difficulty in quite a simple manner, by subjecting the crystal to a steady voltage equal to the peak voltage to be dealt with. By this means, the peak voltage (E) is superimposed on the steady voltage (E), and we get an alternation from 0 to + (E + E) or 0 to − (E + E) instead of from − E to + E, the oscillograph thereby being worked only on one side of zero. This has the objection of raising the new peak voltage to double its previous value, and so rendering the crystal more liable to break down. Usually, however, as explained, the dissymmetry may be ignored.

The rough measurements as to the linear relation were verified by photographing the sine wave of an alternator running at a constant speed (50 cycles/sec.) for different values of R.M.S. voltage, from 0 to 260. The amplitudes of these curves were measured, and a graph drawn showing the relation between the amplitude and the voltage. It was found that, as nearly as could be measured, the graph was linear. Hence, the linear relation may be said to be reasonably satisfied. Most probably the relation holds to a higher degree of accuracy than the measurements made by this method show, but in any case it is sufficiently accurate for the present purpose.

Natural Frequency and Damping.

In order to investigate the natural frequency and damping of the crystal, the automatic switch was arranged so that the crystal was suddenly connected with a source of direct E.M.F. (200 or 400 volts), a photograph being taken at the moment of connexion. If the system is not aperiodic, the sudden shock will set it oscillating in its own period, and damped natural oscillations will appear in the photograph. If, on the other hand, k is not less than $2n$, the resulting photograph will show no trace of free oscillations.

It was found that the oscillograms varied considerably for different crystals. Some were found to show no trace of free oscillations pointing to high damping, while marked oscillations appeared in others. The curve in fig. 8 (Pl. V.), for example, shows a very well marked oscillation after the sudden application of a potential of 440 volts to the crystal. At first, however, when the crystal was freshly formed, no such oscillations were found in the photograph, and the conclusion then drawn was that all crystals were highly damped. Consequently it was thought that the only way of determining the natural frequency was by some resonance method, and attempts were made to obtain a resonance curve for the crystal.

Alternating E.M.F.'s of frequencies from 150 to about

10,000 were produced by means of a transmitting valve, whose grid and plate circuits were coupled by means of large air-core inductances having variable condensers in parallel with one or both for controlling the frequency. R.M.S. voltages of from 70 to 300, as measured by an electrostatic voltmeter, were obtained in this way. Lower frequencies down to 50 were obtained from A.C. generators running at various speeds. These voltages of various frequencies were applied to the crystal, the corresponding curves photographed, and their amplitudes measured. By dividing the amplitude obtained by the voltage for the particular curve, a measure of the amplitude scale for the frequency employed was obtained, and a graph was plotted showing its variation with the frequency. Great trouble was experienced in these experiments owing to the breakdown of the crystals (referred to later) which frequently required a fresh start to be made with new ones, and for this reason no complete curve was obtained at this stage. Evidence was obtained, however, of the existence of a resonance peak usually at a frequency of about 3000, and of a minimum between the peak and zero. From this it will be seen that the system cannot be a simple one as is assumed in the theory, for the curves shown in fig. 1 were plotted on this assumption, and in no case does such a minimum appear. No definite reasons for this behaviour have yet been found. Later attempts at obtaining a resonance curve met with more success, but the results obtained are not complete enough for publication at present.

Some possible explanations of the peculiar form of the resonance curve are, however, suggested, viz.:—

1. The internal damping may be a function of the frequency.
2. The hysteresis effect observed by Valasek may play some part in the matter.
3. The electrical properties of the crystal may vary with the frequency (*e.g.*, the S.I.C. becomes large at resonant frequency, and then swings round to a negative value, as observed by J. G. Frayne) *.

These suggestions have not yet been fully inquired into, and further work in this direction might lead to interesting results.

The photographs showing free oscillations were not obtained with crystals less than a few months old. It was observed that they were only given by crystals which had been standing idle for a long time. Fresh ones invariably gave no trace of oscillations. Consequently it must be assumed that some sort of seasoning process such as setting or drying had occurred in the meantime, which altered the quality of the crystal. As far as could be judged by the eye however, the crystals had the same appearance whether of the former or latter type.

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* J. G. Frayne, "Reversible Inductivity of Rochelle Salt Crystals," Phys. Rev. March 1923.

The older crystals were found to be much stronger electrically than the fresh ones, although not quite so sensitive. Comparing the two types, it may be stated that when freshly made, crystals are obtained which

1. Behave as if they were strongly damped,
2. Are very sensitive, usually showing suitable deflexions at voltages below 250,
3. Are easily spoilt by electrical breakdown,

and that these crystals, on being left alone, tend to pass to a type in which they are

1. Not strongly damped (not aperiodic),
2. Not so sensitive, usually requiring voltages above 250 for successful operation,
3. Fairly strong electrically,

The advantages of both types are obvious; in practice, the latter type is found to be the more suitable to work with, on account of its comparative freedom from breakdown, but artificial damping has to be applied to render the system aperiodic, and higher voltages must be used. It is quite possible that the crystals pass through a stage in the seasoning process when the damping is just sufficient to make the system aperiodic. If it were possible to keep them in this state, the crystal would be suitable for an oscillograph without artificial damping.

In the case of seasoned crystals, artificial damping is necessary, and the following very simple method was found to be the best way of applying it. A fixed surface is placed beneath and parallel to the metal arm attached to the crystal, and in the narrow space between them a small quantity of vaseline is introduced. By altering the width of the space the thickness of the vaseline film, and so the viscous drag or damping, may be varied (see fig. 7). By careful adjustment the system can be rendered just aperiodic. This method has the advantage of not requiring the moving system to be immersed in oil as is the case in some oscillographs.

Figs. 8 and 9 (Pl. V.) show shock oscillograms for the system undamped and aperiodic respectively. In this particular case the natural frequency was found to be 3190.

Shock curves for the earlier type of crystals obtained resembled fig. 9, showing the presence of some form of internal damping.

It should be noted that the displacement is not instantaneous, although the change of potential is practically so. This may be due to the hysteresis observed by Valasek. The lag varies with different crystals, and the error introduced is not very great as a rule.

In the artificially damped form, we have an oscillograph which is capable of recording voltage oscillations whose working range is from 0 to about 1000 volts. The upper limit is, of course, determined by the strength of the crystal. Higher values than 1000 have been successfully recorded, but the risk of breakdown increases with the voltage.

The frequency range will depend upon the purpose for which the instrument is required. When dealing with a single harmonic applied force, damped or undamped, any frequency *less* than the natural one may be used, provided the amplitude scale for that frequency is known. If two or more components are present however, or if there are harmonics, the frequency of the most rapid vibration to be dealt with should not exceed 0·2 of the natural frequency unless corrections are applied to the curve. Bearing in mind that the natural frequency is usually about 3000, this means that the range will be from 0 to about 600 for compound oscillations, and higher for single oscillations. The instrument would therefore be useful for A.C. engineering, where the fundamental usually lies in the neighbourhood of 50 cycles per second.

The capacity of the average crystal is stated by Nicolson to be from 10^{-9} to 10^{-8} farad, and the A.C. impedance about 200,000 ohms for acoustical frequencies. These values have not yet been verified for the crystals grown by the writer.

The direct current resistance is found to be different according as the girdle is + or −. For a crystal 3 cm. square, the resistances were respectively 4 and 10 megohms, while for a crystal 4 cm. square they were 6·25 and 25 megohms. This dissymmetry was also observed by Nicolson, but he makes no mention of the different values of the deflexion obtained for equal + and − potentials. There is probably some connexion between the two effects.

Bearing in mind the low capacity, and high impedance and resistance, we may regard the instrument as practically electrostatic, and it may be assumed that it will not disturb to any appreciable extent the circuit to which it is connected, especially when the work consists of the analysis of the voltage curves of A.C. machinery.

It is found that if a crystal be subjected for some time to a moderate alternating voltage of a frequency too near the resonant frequency, its impedance will suddenly diminish, and the crystal will allow an appreciable current to pass. If the voltage be maintained, the current may become sufficiently great to heat the crystal and fuse it up, and probably electrolyse it.

When a crystal reaches this stage (referred to before as the breakdown) its sensitiveness is lost, as no amplitude is obtainable. On being left alone for a time, it recovers its sensitiveness, partly or wholly, depending upon the length of time which has elapsed, but it is afterwards much more liable to breakdown than before. The photographs shown were obtained with a crystal that had recovered after about two months. It was for the purpose of protecting the crystals against breakdown, by subjecting them to the voltage for only a very short time, that the automatic switch was used.

Just before breakdown, the sensitiveness increases enormously for a second or two, a loud sound of the same frequency as the E.M.F. being emitted, and then the amplitude falls to zero as the impedance falls. If the spot of light on the screen be watched while this takes place, it is observed that the oscillations are on one side of the zero position. As the crystal approaches breaking-down point, the mean position travels further from the zero while the amplitude increases, until, finally, the crystal breaks down, and the amplitude falls to zero. If the concave mirror be revolving slowly, a curve similar to the "grid leak" rectification curve of wireless is observed on the screen, but, unfortunately, it has not been found possible, for obvious reasons, to photograph this phenomenon.

Provided the resistance in the circuit is sufficient to prevent the crystal from fusing after breakdown, it is found that there is practically no difference in appearance between it and a good crystal ; no cracks or flaws are visible that were not there originally. No explanation can be given of this, but it is possible that some internal disruption takes place. J. H. Morecroft observed a similar effect in the case of a quartz slab, viz. : complete disruption at the resonant frequency with a voltage below the one required to break down the dielectric under normal conditions.

As in the case of quartz, a sound is emitted when a rochelle salt crystal is subjected to an alternating voltage.

This is particularly evident at frequencies of several thousands, and notes can be heard up to the limit of human audibility with a suitable valve oscillator. Such frequencies, however, are liable to break down the crystal. The sound is much louder than in the case of quartz.

Examples of Curves obtained.

The photographs shown in figs. 8 to 15 (Pl. V.) were taken with the object of illustrating the usefulness of the instrument. In all cases the fork frequency was 384.

Figs. 8 and 9, as already explained, are shock oscillograms for a crystal undamped and with artificial damping respectively. These were obtained by changing the potential applied to the crystal suddenly from 0 to 440 volts. If fig. 9 be carefully examined, it will be seen that there is a slight trace of free oscillation recorded at the commencement of the displacement, showing that the damping was just on the point of being sufficient to ensure aperiodicity. The fact that the displacement was not quite instantaneous should also be observed. This has been referred to before.

Fig. 10 shows the curve given by one phase of a 3-phase rotary converter. The R.M.S. voltage was 260. It will be observed that the curve is remarkably free from harmonics—practically a pure sine wave. The frequency, as calculated from the fork scale, which unfortunately is of rather small amplitude in this particular photograph, is 46·9. This curve was given on open circuit, the crystal being simply connected to the two terminals of the machine.

The curve of an inductor alternator (single phase) is given in fig. 11. Owing to the low voltage of the machine (110) a 2–1 step-up transformer was used to raise the voltage before applying it to the crystal. This would, of course, tend to reduce the amplitude of the harmonics. Even so, it will be observed that they are very prominent. The voltage applied to the crystal was 210 R.M.S., and the frequency 109·7.

Fig. 12 gives the open circuit voltage of a high frequency alternator, also of the inductor type, but of different construction to the previous one, intended for wireless work. Here again, the harmonics are in evidence, although the general shape of the curve is different from the previous one. No transformer was used in this case. The R.M.S. voltage was 240 and the frequency 768·0. Comparing these three alternator curves, it will be observed that as the frequency increases, the amplitude scale decreases, as is the case when working on the "$k=2n$" curve. The third curve, fig. 12, was beyond the accurate working range of the instrument for compound curves, assuming the range to be from 0 to about 600, but it serves to show what harmonics are present, although they may not be represented in correct proportion.

A valve oscillation is shown in fig. 13. The plate and grid coils were kept shortcircuited by the switch, until this was opened by the mirror turntable. Oscillations were then built up from zero as shown in the photograph. The voltage when the oscillations were steady was 240 R.M.S. Two valves were used in parallel, and the crystal was connected to the terminals of the tuning condenser. The frequency as calculated from the fork scale is 485·0.

Fig. 14 shows a damped oscillation obtained (as in the primary of an induction coil) by unshortcircuiting a condenser connected in series with an inductance and a battery. The crystal was connected to the terminals of the condenser. The capacity being known, the inductance can be calculated. In this case, the capacity was 0·55 mfd.; the frequency recorded was 964·0, and the damping factor, calculated from the curve, 179·9. From these, after correcting for the damping, the inductance works out to be 0·04913 henry. This arrangement thus furnishes a convenient means of determining self-inductances.

Coupled system oscillations are shown in fig. 15. Here, two similar air-core coils were placed near each other, and tuned by condensers to approximately the same frequency. Oscillations were then set up in one circuit by the same method as for the previous curve, and the variation in the primary voltage recorded. By connecting a second oscillograph to the secondary circuit, and arranging the second spot vertically above the first, it was possible to show the transference of energy from one circuit to another.

It is also possible to use this instrument for the study of sound waves, by connecting a microphone and step-up transformer to the grid circuit of a valve, and connecting the plate of the valve, via another transformer, to the crystal. By this means, curves (not reproduced) have been obtained for organ-pipes, etc. Alternating voltages of about 200 are easily obtained at the terminals of the transformer connected to the crystal by whistling into the microphone.

Conclusion.

From the foregoing results and photographs, it is evident that a piezo-electric oscillograph can be constructed with a rochelle salt crystal. Such an instrument possesses the following favourable properties:—

1. High voltages are not required for operation as is the case in some electrostatic oscillographs.
2. The moving system does not require oil immersion.
3. Owing to its high resistance and impedance, the instrument is practically electrostatic.
4. The instrument has very low capacity.
5. The adjustment is not difficult.
6. The instrument is compact, of simple construction, and of low cost.

A disadvantage is that rochelle salt crystals do not appear to have very high natural frequencies of vibration, the average value for crystals 3 to 4 cm. square being about 3000. The use of the instrument is thus limited to low frequency work, for which it is, however, very suitable, as indicated by the curves described above.

Possibly some other crystal may be found to be more suitable. If sufficient magnification could be obtained, a quartz oscillograph would probably, owing to the very definite physical properties of this substance, be superior to one of rochelle salt.

The present investigation should be regarded as a preliminary study of a new type of instrument, and as indicating its possibilities, rather than as an exhaustive inquiry into the subject. The work in connexion with it was carried out in the Physical Laboratories of the University College of North Wales, Bangor, and the writer desires to thank Dr. Taylor Jones for his valuable assistance and encouragement during the whole of the work.

XXXIV. *Some New Methods for the Measurement of Thermal Conductivity.* *By* T. Barratt, *D.Sc., and* R. M. Winter, *M.Sc., Research Department, Royal Arsenal, Woolwich* [*].

I.

In a paper on "Thermal and Electrical Conductivities of some of the rarer Metals and Alloys" it was shown by one of us [†] that the thermal conductivity k of a thin rod could be expressed by the formula

$$k = \frac{H^2}{pqhV^2} \coth^2 \alpha l,$$

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[*] Communicated by the Authors. This paper is published by permission of the Director of Artillery.

[†] T. Barratt, Proc. Phys. Soc. xxvi. (5), pp. 347-371 (1914).

where the symbols have the meanings given in Section III. When l is great, the formula reduces to the very simple expression

$$k = \frac{H^2}{pqhV^2}.$$

Apart from the simplicity of the formula, the arrangement adopted had the advantage of a "null method" for the measurement of H, and could be used for a very small sample of wire in the case of a rare metal or alloy. The same formula and arrangement of apparatus were also successfully employed for such bad conductors as glass, various woods, ebonite, and firebrick.

II. *Measurement of the Emissivity "h."*

The most troublesome and uncertain part of the necessary measurements employed in the use of the formulæ given above is that of h, the emissivity of the rod or wire. The value of h depends on the temperature of the enclosure, increasing from 0·000533 at 17° C. to 0·000634 at 100° C. for wires of 1 mm. diameter used by the author [*]. It also varies appreciably if the rod is raised more than about 10° C. above the temperature of the enclosure. Prof. C. H. Lees [†], in the case of rod 5·85 mm. in diameter, obtained the values 0·000126, 0·000160, and 0·000200 at temperatures $-155°$, $-64°$, and 23° C. respectively; while one of us [‡], for a rod of about the same dimensions, found an increase from 0·000224 at 18° C. to 0·000265 at 100° C. Lees points out that none of the formulæ suggested up to the present (1908) to express the variation of h with the temperature t fitted his results. He himself gave the relation $h = 1 - bt^{3/2}$ (where b is a constant) for the case of a small rod at very low temperature in an enclosure only a few, say 10, degrees cooler than itself.

There seems to be little doubt, however, that the value of h depends on other factors besides the temperature. For example, the dimensions and shape of the heated body and those of the enclosure, as well as the temperature excess of the heated rod, will certainly have an effect, probably considerable, on the value of h. The emissivity of a thin rod or wire heated in air has been shown to depend chiefly upon convection [§]. The relative proportions of radiation (including conduction) and convection vary considerably, however, with the diameter of the rod or wire and with the nature of its surface. For example, in the case of a metal wire of 1 mm. in diameter it was shown that of 100 parts of "total heat" lost from the wire at 12° C., only 2·5 consist of radiation for a bare wire and 12·6 for a blackened wire, the remainder being due to natural or free convection. At 100° C. these percentages become 4·4 and 20·7 respectively, the wire in each case being heated not more than 10° C. above the temperature of the enclosure in which it was placed. For a cylinder of about 5 mm. diameter, the percentage of radiation was found to be 10 for the bare surface and 37 for the blackened surface *.

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[*] T. Barratt, Proc. Phys. Soc. xxvi. (5), pp. 347–371 (1914).

[†] C. H. Lees, Phil. Trans. A, ccviii. p. 205 (1908).

[‡] T. Barratt, Proc. Phys. Soc. xxvii. pp. 81–93 (1914).

[§] T. Barratt, Proc. Phys. Soc. xxviii. pp. 1–13 (1915).

In the experiments referred to in Section I., h had to be measured in a separate experiment under conditions as nearly as possible similar to those employed in the main experiment. The assumption was made that the value of h was the same in both cases. If it was required to measure k at different temperatures, it was necessary to measure h separately for each temperature.

It would be preferable, therefore, to eliminate h entirely from the formulæ; and it is proposed in this paper to develop expressions for the thermal conductivity k which do not involve a separate measurement of h †. This will be done first as a general proposition, the formula being applicable to any material, and avoiding certain approximations made in the paper referred to in Section I. Thereafter certain particular cases will be considered which are of experimental interest. An expression for the calculation of h itself will also be given. (See Section III., 6.)

III. *Expressions for the Thermal Conductivity* "*k*."

The propositions to be dealt with are as follows:—

(1) To find the thermal conductivity k from measurements of the dimensions of the rod, the amount of heat supplied per second, the temperature of the hot end, and the temperature of one other point on the rod.

(2) A particular case of (1), applicable only when the rod is long.

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* T. Barratt and A. J. Scott, Proc. Phys. Soc. xxxii. pp. 361-373 (1920).

† They do involve, however, an additional measurement of temperature at some point on the rod itself.

(3) A particular case of (1), applicable to many metallic systems, and leading to the approximate expressions of Section I.

(4) To find k, given the dimensions of the rod, the amount of heat supplied to one end per second, and the temperatures of the two ends.

(5) To find k, given the ratio of the heat supplied to the temperature of the hot end for two different lengths of the same rod.

(6) To find the emissivity h directly, given the same data as in (4) above.

The experimental conditions are assumed to be similar to those used in the paper referred to in Section I.

The quantities used in the calculations are defined as follows:—

l = length of the rod, in cms.
r = radius of a rod of circular cross-section, in cms.
q = area of cross-section, in cms.
p = perimeter of the rod, in cms.
h = emissivity of the rod surface—*i. e.*, the number of calories emitted per sq. cm. per degree cent. of temperature difference.
k = coefficient of thermal conductivity of the material.
$\alpha = \sqrt{hp/qk}$.
H = the number of calories supplied per second to the hot end of the rod.
V = the temperature difference in degrees cent. between the hot end of the rod and its surroundings.
V′ = the same, for the cold end of the rod.
v = the temperature difference between a point x cms. from the hot end of the rod and the surroundings.

(1) *To find k, given p, q, l, H, V, v, and x.*

The general equation for the fall of temperature along a rod in the condition specified is

$$\frac{d^2v}{dx^2} = \frac{hp}{qk}v = \alpha^2 v, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)^*$$

of which a general solution is

$$v = A\cosh \alpha x + B\sinh \alpha x, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where A and B are constants.

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[*] "h" is assumed to be constant in this equation, and the method given below will only hold for cases in which the fall of temperature along the rod is limited to a few degrees.

To determine the values of A and B, put $x=0$;

$$\text{then } v=V, \quad \text{and therefore } A=V.$$

Also when $x=0$,

$$H = -kq\left(\frac{dv}{dx}\right); \quad \therefore \frac{dv}{dx} = -\frac{H}{kq},$$

and by differentiating (2),

$$\frac{dv}{dx} = \alpha A \sinh \alpha x + \alpha B \cosh \alpha x$$

$$= \alpha B \quad \text{when} \quad x=0.$$

Hence
$$\alpha B = -\frac{H}{kq}.$$

$$\therefore \quad B = -H/kq\alpha;$$

$$\therefore \quad v = V \cosh \alpha x - \frac{H}{kq\alpha} \sinh \alpha x \quad . \quad . \quad . \quad (3)$$

and
$$\frac{dv}{dx} = \alpha V \sinh \alpha x - \frac{H}{kq} \cosh \alpha x. \quad . \quad . \quad . \quad (4)$$

Now put $x=l$. Then $v=V'$; so that

$$V' = V \cosh \alpha l - \frac{H}{kq\alpha} \sinh \alpha l \quad . \quad . \quad . \quad . \quad (5)$$

and
$$\frac{dv}{dx} = \alpha V \sinh \alpha l - \frac{H}{kq} \cosh \alpha l. \quad . \quad . \quad . \quad . \quad (6)$$

But when $x=l$, the heat transmitted by conduction through the end layer of the rod is identical with that emitted from the surface of that end.

Therefore when $x=l$,

$$-kq\frac{dv}{dx} = hqV';$$

i. e., when $x=l$,

$$\frac{dv}{dx} = -\frac{hV'}{k} = -\frac{hp}{qk} \cdot \frac{qV'}{p} = -\frac{q\alpha^2}{p} \cdot V'$$

Substituting from (5) and (6),

$$\alpha V \sinh \alpha l - \frac{H}{kq} \cosh \alpha l = -\frac{q\alpha^2}{p}\left(V \cosh \alpha l - \frac{H}{kq\alpha} \sinh \alpha l\right).$$

Multiplying throughout by pkq sech αl,

$$pqk\alpha V \tanh \alpha l - pH = -kq^2\alpha^2 V + q\alpha H \tanh \alpha l,$$

which on rearrangement gives

$$k = \frac{H}{q\alpha V} \cdot \frac{q\alpha \tanh \alpha l + p}{q\alpha + p \tanh \alpha l} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

or

$$k = \frac{H}{q\alpha V} \cdot \coth\left(\alpha l + \tanh^{-1}\frac{q\alpha}{p}\right). \quad . \quad . \quad . \quad (8)$$

From (3),

$$kq\alpha v = kq\alpha V \cosh \alpha x - H \sinh \alpha x\ ;$$

$$\therefore \quad k = \frac{H}{q\alpha V} \cdot \frac{\sinh \alpha x}{\cosh \alpha x - v/V}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Combining (8) and (9), we have the relation

$$\frac{\sinh \alpha x}{\cosh \alpha x - v/V} = \frac{q\alpha \tanh \alpha l + p}{q\alpha + p \tanh \alpha l} \quad . \quad . \quad . \quad . \quad (10)$$

$$= \coth\left(\alpha l + \tanh^{-1}\frac{q\alpha}{p}\right). \quad . \quad (11)$$

Now, while an explicit expression for α cannot be obtained, it is quite a simple matter to evaluate it graphically. All the quantities are known except α ; so that, by giving α a few arbitrary values, it is possible to plot out the curves

$$\frac{\sinh \alpha x}{\cosh \alpha x - v/V} = f(\alpha), \quad \text{and} \quad \frac{q\alpha \tanh \alpha l + p}{q\alpha + p \tanh \alpha l} = F(\alpha),$$

and this may be done with any degree of precision. The value of α at the point of intersection of the two curves is the value which satisfies the relations (10) and (11). The other coordinate at the point of intersection gives the value of $f(\alpha)$ or $F(\alpha)$ at that point. The value of k now follows by simple substitution in (9).

It will be observed that this solution is quite general, and does not involve the measurement of h. A numerical example will illustrate the method.

Example :—

A cylindrical wire 10·00 cm. long and 2 mm. thick is placed in a constant temperature enclosure and heated at one end at the rate of $6{\cdot}290 \times 10^{-3}$ calorie per second. When equilibrium is reached, the hot end is found to be 5°·00 C. hotter than the enclosure, while at a point 7·31 cm. from the hot end the temperature is 0°·83 C. above that of the enclosure.

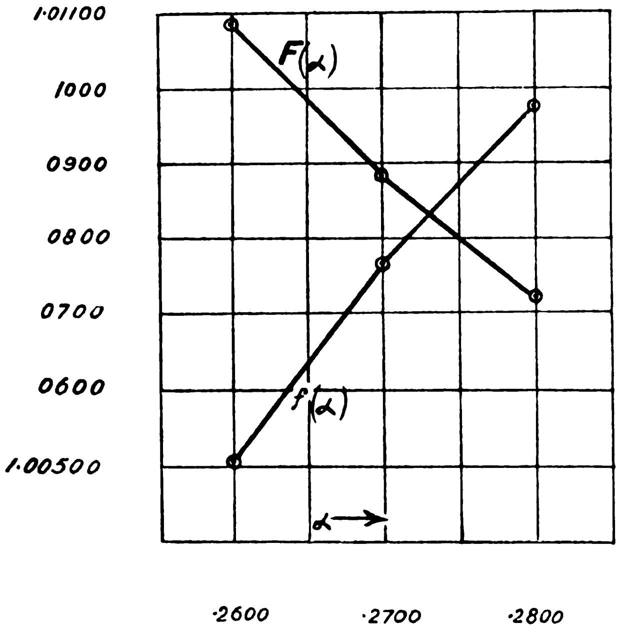
We have the following data :—

$r=0{\cdot}100$, $p=0{\cdot}6283$, $q=0{\cdot}03142$, $l=10{\cdot}00$,

$H=6{\cdot}290\times10^{-3}$, $V=5^{\circ}{\cdot}00$ C., $v=0^{\circ}{\cdot}83$ C., $x=7{\cdot}31$.

TABLE of values of α, $f(\alpha)$, and $F(\alpha)$.

a.	qa/p.	ax.	al.	cosh ax.	sinh ax.	$f(a)$.	tanh al.	$F(a)$.
·2600	·0130	1·9006	2·6000	3·4197	3·2702	1·00508	·98903	1·01081
·2700	·0135	1·9737	2·7000	3·6681	3·5292	1·00773	·99101	1·00883
·2800	·0140	2·0468	2·8000	3·9361	3·8070	1·00977	·99263	1·00722



The two curves intersect at the point $\left\{\begin{array}{r} \alpha = \ {\cdot}2728 \\ f(\alpha)=1{\cdot}00835 \end{array}\right\}$ (see Curve), from which it follows, since $k=\frac{H}{q\alpha V}\cdot f(\alpha)$, that

$$k=\frac{6{\cdot}290\times10^{-3}\times1{\cdot}00835}{0{\cdot}031416\times0{\cdot}2728\times5},$$

$$k=0{\cdot}148(0).$$

We now proceed to two particular cases of the above.

(2) *A particular case of* (1) *when l is large.*

When l is great, $\tanh \alpha l$ approximates to unity, and it follows from (7) that $k=\frac{\mathrm{H}}{q\alpha\mathrm{V}}$.

Hence by (10),
$$\frac{\sinh \alpha x}{\cosh \alpha x - v/\mathrm{V}}=1;$$

$$\therefore \quad v/\mathrm{V}=\cosh \alpha x-\sinh \alpha x=e^{-\alpha x};$$

$$\therefore \quad \alpha x=\log_e (v/\mathrm{V});$$

$$\therefore \quad \alpha=-\frac{1}{x}\log\frac{v}{\mathrm{V}}=\frac{1}{x}\log\frac{\mathrm{V}}{v}.$$

$$\therefore \quad k=\frac{\mathrm{H}}{q\alpha\mathrm{V}}=\frac{\mathrm{H}x}{q\mathrm{V}\log_e\frac{\mathrm{V}}{v}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

a very simple expression, independent of h, and requiring the measurement of the heat H given to one end of the rod, the temperature V at that end, the cross-sectional area of the rod, and the temperature v at a point distant x from the hot end.

(3) *A particular case of* (1), *assuming $h/k\alpha$ is small.*

It was shown in a former paper (*loc. cit.*) that for a great many thin metallic rods the quantity $h/k\alpha$ is very small, the error involved in neglecting it being less than one part in ten thousand. Making this approximation, we have

$$\frac{q\alpha}{p}=\frac{q\alpha^2}{p\alpha}=\frac{q}{p\alpha}\cdot\frac{hp}{kq}=\frac{h}{k\alpha}=0.$$

Therefore, substituting in (8) and (11),

$$k=\frac{\mathrm{H}}{q\alpha\mathrm{V}}\coth \alpha l \quad . \quad . \quad . \quad (13)$$

and
$$\frac{\sinh \alpha x}{\cosh \alpha x - v/\mathrm{V}}=\coth \alpha l. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

This greatly simplifies the graphical solution of (11). It will be observed that in the numerical example given above the tabulated values of F(α) are very nearly the reciprocals of those of $\tanh \alpha l$. The error involved in writing $\mathrm{F}(\alpha)=\coth \alpha l$ would be only 0·2 per cent. of the value of k.

The formula quoted at the beginning of this paper follows directly from the relation

$$k=\frac{\mathrm{H}}{q\alpha\mathrm{V}}\coth\alpha l,$$

for
$$k^2=\frac{\mathrm{H}^2\coth^2\alpha l}{q^2\alpha^2\mathrm{V}^2}$$

$$=\frac{\mathrm{H}^2\coth^2\alpha l}{q^2\frac{hp}{qk}.\mathrm{V}^2}=k\frac{\mathrm{H}^2\coth^2\alpha l}{pqh\mathrm{V}^2}.$$

$$\therefore\qquad k=\frac{\mathrm{H}^2}{pqh\mathrm{V}^2}.\coth^2\alpha l.\qquad\qquad(15)$$

(4) *To find "k" from measurements of q, l,* H, V, *and* V′, *with the assumption as in* (3) *that the quantity qα/p is small.*

From (14)
$$\frac{\sinh\alpha x}{\cosh\alpha x-v/\mathrm{V}}=\coth\alpha l.$$

When
$$x=l,\text{ and }v=\mathrm{V}',$$

$$\sinh^2\alpha l=\cosh^2\alpha l-\frac{\mathrm{V}'}{\mathrm{V}}\cosh\alpha l;$$

$$\therefore\qquad\frac{\mathrm{V}'}{\mathrm{V}}\cosh\alpha l=\cosh^2\alpha l-\sinh^2\alpha l=1.$$

$$\therefore\qquad\cosh\alpha l=\frac{\mathrm{V}}{\mathrm{V}'}.\qquad\qquad(16)$$

$$\therefore\qquad\alpha=\frac{1}{l}\cosh^{-1}\left(\frac{\mathrm{V}}{\mathrm{V}'}\right),\qquad\qquad(17)$$

while
$$\sinh\alpha l=\frac{\sqrt{\mathrm{V}^2-\mathrm{V}'^2}}{\mathrm{V}'}\text{ and }\coth\alpha l\frac{\mathrm{V}}{\sqrt{\mathrm{V}^2-\mathrm{V}'^2}}.\qquad\qquad(18)$$

Since (13),
$$k=\frac{\mathrm{H}}{q\alpha\mathrm{V}}\coth\alpha l,$$

by (17) and (18)
$$k=\frac{\mathrm{H}}{q\mathrm{V}}\cdot\frac{l}{\cosh^{-1}(\mathrm{V}/\mathrm{V}')}\cdot\frac{\mathrm{V}}{\sqrt{\mathrm{V}^2-\mathrm{V}'^2}}$$

or
$$k=\frac{\mathrm{H}l}{q\sqrt{\mathrm{V}^2-\mathrm{V}'^2}.\cosh^{-1}(\mathrm{V}/\mathrm{V}')}.$$

(5) *To find "k," given the ratio* H/V *for two values of l.*

Since $$\frac{H_1}{qaV_1}\coth al_1 = k = \frac{H_2}{qaV_2}\coth al_2,$$

k can be found graphically in a manner entirely analogous to that used in I. (1) by plotting the two functions $\frac{H}{q\alpha V}\coth \alpha l$ against α and taking their value at their point of intersection.

(6) *To find "h," given p, q, l,* H, V, *and* V′, *when* $\frac{qc}{p}$ *is small.*

Since by definition $a^2 = \frac{hp}{kq}$.

$$\therefore \qquad hp = q\alpha^2 k,$$

which by (13)

$$= q\alpha^2 \frac{H}{q\alpha V}\coth \alpha l = \frac{H\alpha \coth \alpha l}{V}.$$

Therefore by (17) and (18),

$$h = \frac{H}{pV} \cdot \alpha \coth \alpha l$$

$$= \frac{H}{pV} \cdot \frac{1}{l}\cosh^{-1}\left(\frac{V}{V'}\right) \cdot \frac{V}{\sqrt{V^2 - V'^2}}$$

or $$h = \frac{H \cosh^{-1}(V/V')}{pl\sqrt{V^2 - V'^2}}.$$

In Section III. (4), (5), and (6), perfectly general solutions making no restriction on the magnitude of $q\alpha/p$ are readily available by the same method, but the forms obtained are rather involved.

Our thanks are due to Prof. C. H. Lees for kindly advice and criticism.

XXXV. *The Thermal Theory of Gas Ignition by Electric Sparks.* *By* J. D. MORGAN, *M.Sc.* *

Introduction.

THE main purpose of this paper is to examine the thermal theory of gas ignition by electric sparks in the light of experimental results. The theory asserts that ignition depends on the raising of a sufficient volume of the combustible gas to a sufficient temperature. Two quantities only are involved in the theory—volume and temperature. No account is taken of chemical or material changes in the process of ignition. The justification for the reference to volume is that a spark insufficient to initiate combustion of the whole of the gas will burn some of the gas immediately adjacent to the spark, but the flame does not spread. It appears to be necessary to ignite a sufficient quantity of the gas to ensure autogenous ignition of the whole. From the theory as stated, it follows that to cause ignition requires a definite amount of heat to be imparted to a definite volume of the gas. If that volume could be raised instantly and uniformly to the ignition temperature, without loss of heat to the surrounding gas, the amount of heat necessary to cause ignition would be the minimum. Experimental results can only approximate to the ideal minimum, and the degree of approximation will depend on conditions associated with the experiment. Diversity of results is therefore inevitable.

The fact that the subject of spark ignition is associated with experimental results of great diversity forms the basis of the opinion held by some, that but little if any satisfactory information exists on the subject. It is not generally understood, however, that diversity as regards the energy required to cause ignition is inevitable, and is at the same time consistent with the simple hypothesis above enunciated.

By means of the thermal theory much of the perplexity which surrounds the subject of spark ignition is caused to disappear, and apparently discordant results are co-ordinated. There is no alternative theory of which the same can be stated. The suggestion has been made that ignition depends upon some form of electrical activity which cannot be expressed in terms of energy, but the suggestion does not appear to have been developed. It is not denied that the interaction of the spark and gas may be electrical in character. This possibility is not excluded by the thermal theory, any more than is an electrical theory of flame excluded by the science of thermodynamics.

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* Communicated by Prof. E. Taylor Jones.

Experimental limitations.

Before a clear conception of the subject can be formed it is necessary to know something of the experimental limitations. The supposition that ignition is an operation depending on the transference of energy to the gas from the spark in the form of heat is not unreasonable. Until the supposition is proved to be false, measurements of energy, or of factors involved in appropriate energy expressions, afford the natural means of investigation. It will be obvious that three measurements are conceivable, though it will be apparent that only two are possible. As a result of the spark a temperature wave travels from the spark throughout the gas. Ignition follows from a transient condition in which the heat given up by the spark is localized in the region surrounding the spark. A direct attack upon the problem would involve a measurement of the heat concentrated in the gas region adjacent to the spark immediately prior to ignition, but this is impossible. A practicable method is to measure the heat given up by the spark, the heat being imparted for the purpose of measurement to a non-inflammable gas. Only the final effect of the heating can be measured in this way,—not the transient condition on which ignition depends. The method has been used. It is inconvenient, and possesses no advantages, except as a check, over the other and third method which is the one ordinarily employed. This consists in measuring the energy (or a suitable factor of the energy) available for spark production in the apparatus used for generating the spark.

The use of the energy available for spark production as a criterion of incendivity (or ability of the spark to cause ignition) involves several arbitrary assumptions. It tends to produce a crop of misleading results, and depends more on necessity than choice. Nevertheless, provided its limitations are always kept in view, the method is of great value, and by its aid a clear appreciation of the conditions affecting ignition becomes possible.

The sparks used in ignition experiments are divided into two classes, inductance and capacity sparks. Inductance sparks are obtained between a pair of contacts when the current flowing in an inductive circuit is interrupted by separation of the contacts. Capacity sparks result from the discharge of an electrostatic condenser across a gap between a pair of electrodes. The energy available for the production of an inductance spark is equal to $\frac{1}{2}Li^2$, where L is the inductance of the circuit and i the current flowing prior to interruption. For a capacity spark, $\frac{1}{2}CV^2$ is the measure of the energy available for spark production, C being the capacity of the condenser and V the sparking voltage of the gap. The use of either measurement involves the assumption that the whole or the greater part of the energy available is discharged in the spark. Under suitable experimental conditions a great, if not the greater, part of the energy undoubtedly appears in the spark, and the proportion is sufficiently definite and constant to justify the use of available energy as a measure (for comparative purposes) of actual spark energy. But under unfavourable experimental conditions the assumption leads to anomalous results; examples of such conditions are given in the later portion of this paper.

Principal causes of Spark Energy Variations.

Assuming satisfactory experimental conditions, diversity in the spark energy required to cause ignition of a given gas results mainly from one or both of two conditions. The one depends on the rate at which the heat is imparted to the gas, the other on the manner in which the electrodes, between which the spark is formed, interfere with the efficient distribution of heat in the gas adjacent to the spark.

Effect of rate of imparting Heat from Spark to Gas.

The heating of the gas to the condition required for ignition involves time. During this time heat is accumulating in the region around the spark, and some is also passing uselessly to the remoter portions of the gas. At the instant of ignition the temperature distribution in the gas around the spark is not uniform. Of the quantity of heat given by the spark to the gas, the amount that is effectively employed in causing ignition will depend on the rate at which the heat is imparted. This aspect of the problem has been examined theoretically in a previous paper *. In that paper the problem was reduced to one of examining the heating effect of different point sources of heat on air, the heat being communicated from the source to the air by conduction only. The calculations showed that the effectiveness of a given quantity of heat in raising a given volume of gas to a given temperature depends essentially on the manner in which that heat is communicated to the gas. When the heat is imparted instantaneously to a point source, the boundary of a larger volume of gas is raised to a given temperature than when the same quantity of heat is imparted at a uniform rate over a finite interval of time. For example, the heating effect of a point source of total heat of 0·001 calorie uniformly in action over 0·005 sec. (continued heat source) was about 17 per cent. less than that of an instantaneous point source of the same total heat. In the calculations it was assumed that the different point sources of heat were surrounded entirely by gas.

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* "On the form of the temperature wave spreading by conduction from point and spherical sources; with a suggested application to the problem of spark ignition." Taylor Jones, Morgan & Wheeler, Phil. Mag. vol. xliii. Feb. 1922.

It is difficult, indeed it appears impossible owing to the complex conditions which exist in the ignition of a gas by a spark, to test directly the conclusions arrived at in that paper, although it is known that, in general, the incendivity of inductance sparks (which can be regarded as continued heat sources) is less than that of capacity sparks (which can be regarded as instantaneous heat sources). For example, in some experiments, the least energy by which ignition of an 8·5 per cent. methane-air mixture could be obtained by a capacity spark was ·002 joule. That for an inductance spark was ·006 joule. It is not possible, however, to state whether the difference was due wholly or only in part to the rate of heating, because both results depend to some extent on the "electrode effect" described below. The general conclusions arrived at in the earlier paper are, however, equally applicable to another ignition problem in connexion with which they are easily tested in a direct manner. For the ignition of explosives in blasting operations, electrically fired fuseheads are commonly used. A fusehead consists of a solid globule of readily ignitible material in which is embedded a very fine and short wire. Ignition of the fusehead is effected by passing an electric current through the wire. Experiments on the ignition of fuseheads are very much simpler than those on the ignition of gases, as the conditions are more definite. In the experiments to be mentioned the object was to find the current required for ignition when the duration of current was limited to a definite interval of time. The results obtained in one set of experiments on fuseheads of 1 ohm resistance are given below :—

Duration of current. sec.	Igniting current. amp.	Energy required for ignition. $C^2R.t.$
·1	·38	·0144
·08	·4	·0128
·06	·415	·0103
·04	·44	·0077
·03	·48	·0069
·02	·53	·0056
·01	·66	·0044
·005	·89	·004

The results when plotted give a straight line relationship between W and t, where W = energy and t = time. Calculations made by Prof. E. Taylor Jones, based on the assumptions made in the previous paper, also show that the relation between W and t should (in the case of a point source) be linear over the same range of values of t[*] as that in the above table. The results obtained in the fusehead experiments therefore agree well in this respect with the thermal theory of ignition.

There appears to be no reason for supposing that, as a thermal operation, the heating of a combustible gas by a hot vapour is essentially different from the heating of a combustible solid by a hot wire. In view of the direct evidence cited, and the absence of evidence to the contrary, it must be regarded as established that the effectiveness of a spark as an igniting agent depends on the rate at which it imparts heat to the gas, and that the differences which are known to exist between the incendivities of capacity and inductance sparks are due in part to this cause.

Electrode Effect.

In the light of the calculations of the first paper, another aspect of the subject has been treated experimentally[†]. The object was to find what modifying effect could be attributed to the presence of electrodes on the heat required to cause ignition of the gas, ignition being initiated by a spark in the region between the electrodes. It was found that the effect of the electrodes on the spark energy necessary for ignition was very great. Using capacity sparks (which can be regarded as instantaneous heat sources) and rather blunt electrodes presenting hemispherical surfaces to the gap, ·007 joule was required to cause ignition of an 8·8 per cent. methane-air mixture when the gap width, or distance between the electrodes, was 0·31 inch. Increasing the gap width to ·055 inch, and thereby increasing the volume of gas between the electrodes, the energy required for ignition was only ·002 joule. It was found that the relationship between these and intermediate figures was consistent with calculations derived from those of the previous paper. Changes in the shape of the electrodes were also accompanied by consistent variations in the energy required for ignition. Change of material appeared to have no effect, as might be expected. The experiments described in the second paper established a fact of great practical importance, namely, that the presence of electrodes can cause very large variations in the amount of heat energy necessary for the ignition of a given gas. They also show that such variations accord with the supposition that ignition depends upon a thermal process.

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[*] The calculations show that at very small values of t the energy W varies slightly less rapidly than according to the linear relation which holds at larger values.

[†] "Some observations on the ignition of combustible gases by electric sparks," J. D. Morgan, Phil. Mag. vol. xlv. May 1923.

Inductance Sparks.

More recently the problem has been examined from various other view points with inductance sparks. It is known that the incendivity of such sparks is lower than that of capacity sparks. This is attributable to two causes. In the first place, the sparks are of appreciable duration and are therefore less efficient as heating agents than the approximately instantaneous capacity sparks. In the second place, the sparks are initiated in a much more confined or restricted gas region than capacity sparks. Stated otherwise, the electrode effect may be much greater in the one case than the other; although it should be mentioned that when capacity sparks are produced between electrodes which are very close together the energy required for ignition approaches very nearly, and has been found to exceed, that necessary with inductance sparks. For example, as already stated, the energy required in a capacity spark formed in a gap of ·031 inch wide, to ignite an 8·8 per cent. methane-air mixture, was ·007 joule. Ignition of the same mixture with an inductance spark has been obtained with a spark energy of as low as ·006 joule. But by slowing down the rate of break, or by increasing the area of adjacent electrode surfaces, this figure can be greatly increased owing to increase of electrode effect. It can also be increased by making the rate of break very rapid; the electrode effect is then reduced to the minimum, but the energy that actually appears in the spark is diminished, owing apparently to premature extinction of the spark. But when an inductance spark produced under optimum conditions is compared with a capacity spark also produced under optimum conditions, the energy required for ignition by the inductance spark is greater than that required by a capacity spark.

The energy required to produce an inductance spark is represented by the quantity $\frac{1}{2}Li^2$. It is important to consider what results are to be expected from experiments in which

L and i are varied, the rate of separation of the contacts and the composition of the gas mixture being kept constant. As a matter of observation, it is known that the sparks required to ignite a given gas vary but little in length and, consequently, in duration over a fairly wide range of variation of L and i. With large differences in L (and corresponding differences in i) there is an appreciable difference in the length of the sparks, the sparks obtained with the larger values of L being longer and less bright than those obtained with small values of L. Considering first the condition in which there is no appreciable variation of spark length and duration: if the thermal hypothesis is correct, then, under that condition, the product $\frac{1}{2}Li^2$ should remain constant, because the mean rate at which heat is generated in the spark is then constant. This conclusion is in accordance with experiments *. Recently the matter has been re-examined, using two air-core coils of different inductance. The gas was a methane-air mixture of 8·5 per cent. methane. The contact breaker consisted of a small flexible phosphor-bronze blade which could be brought into contact with one face of a fixed contact of wedge-shaped section, and after slight flexure could flick past the edge of the fixed contact. This simple device enabled a constant rate of break to be obtained very conveniently. The results were as follows:—

Inductance of coil (L).	Current prior to break (i).	Energy to provide igniting sparks ($\frac{1}{2}Li^2$).
(1) ·02144	·77	·00635
(2) ·012	1·025	·00630

In these experiments the difference between the two inductances is not nearly so large as the differences employed in the earlier experiments, but is sufficient to establish the point under consideration.

In the other condition, in which there are appreciable differences in the spark lengths (and consequently durations), the experimental conditions are obviously more complicated. The greater brightness of the shorter sparks indicates a more rapid rate of heat generation. If this were the only differentiating feature in the experiments, the product $\frac{1}{2}Li^2$ should have been less with a small value of L than with a large value. On the other hand, the longer sparks obtained with the larger values of L should have been more effective on account of the diminution of electrode effect, and the product $\frac{1}{2}Li^2$ should have been less with the large values of L than with the small values. Actually, in the first experiments cited, it was found that with very large differences of L the product $\frac{1}{2}Li^2$ remained constant, due, no doubt, to the fact that differences in the rate of heating were accompanied by counteracting differences in the electrode effect.

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* "The ignition of explosive gases by electric sparks," J. D. Morgan, Trans. Chem. Soc. 1919, vol. cxv.

In some recent experiments with inductance sparks by Prof. R. V. Wheeler, the following figures were obtained in the ignition of an 8·5 per cent. methane-air mixture.

Applied volts.	Inductance, henry.	Igniting current, amp.	Spark energy, ($\frac{1}{2}Li^2$) joule.
90	·031	·42	·0027
„	·063	·26	·0021
„	·095	·19	·0017
30	·063	·35	·0038

It will be noticed that the results differ from the writer's in that the energy required for ignition is much smaller, and the product $\frac{1}{2}Li^2$ diminishes with increase of inductance. It will also be noticed that at the lower applied voltage (30) the spark energy with an inductance of ·063 henry rises from ·0021 to ·0038. In the author's experiments the applied voltage was 4. The two sets of results are hardly comparable, for the reason that the high voltage used in Wheeler's experiments causes considerable energy to be given to the spark which is not included in the quantity $\frac{1}{2}Li^2$. This point is discussed later. For comparison with Wheeler's results, the following obtained recently by the author, in experiments on 8·5 per cent. methane-air mixture with high impressed voltage, are of interest.

Impressed volts.	Inductance, henry.	Igniting current, amp.	Spark energy ($\frac{1}{2}Li^2$).
(1) 220	·02144	·35	·00130
(2) 220	·012	·4	·00096

Here the spark energy increases with increase of inductance. The fact that the variation is the reverse of Wheeler's is no doubt due to some difference in the experimental conditions. Whatever the explanation, the results obtained with high impressed voltage afford no evidence for or against the thermal theory, for the reason already given. The results obtained in experiments with low impressed voltage show that the behaviour of inductance sparks accords with the thermal theory of ignition.

Inductance Sparks produced in Alternating Current Circuits.

In consequence of the work of Thornton there is a widespread belief that sparks produced in alternating current circuits are much less effective in causing ignition than sparks produced in direct current circuits. It has been alleged that his experiments disprove the thermal theory of ignition, and it has also been advocated that where danger from gas ignition is to be anticipated, it is preferable to employ alternating current on account of the wider margin of safety that it is supposed to give. The matter is of great practical importance, and it also has an important bearing on the theoretical aspect of the subject of spark ignition. It is quite easy to show that the belief is without foundation in fact. A small alternator giving a good sine wave was arranged in a circuit containing the ignition apparatus, an air-core inductance coil, a resistance, and a hot wire ammeter. Provision was made for including in series with the circuit a small accumulator as a source of direct current. In the direct current experiments, the alternator rotor was fixed in the position of maximum inductance, and the current from the battery was adjusted until the spark obtained on breaking the circuit was able to ignite the gas. Subsequently the battery was removed from the circuit and current was generated by the alternator, the resistance of the circuit remaining the same. The excitation of the alternator was varied until the least igniting spark was obtained. The flick contact-breaker above mentioned was actuated by hand, and consequently the necessary coincidence of the break with the peak of a current-wave was a matter of chance. But by repeated trials and frequent changes of gas in the explosion-chamber, the least current required to produce an igniting spark was determinable without great difficulty. The procedure may appear to be crude, but actually it is free from the possibility of any serious error. The results of experiments on an 8·5 methane-air mixture were as follows :—

Direct current required to produce igniting spark ·415 amp.

Alternating current required to produce igniting spark :—

Periodicity.	r.m.s. current.	Peak current.
68	·29 amp.	·41
200	·3 „	·42

It will be apparent that the results for alternating and direct current are practically the same. The arrangement of the experiment was such as to insure as nearly as possible identical conditions for the two currents. With the alternator running there was no doubt a small variation in the effective inductance of the generating windings, and this probably accounts for the small differences found in the igniting currents. The experiments establish the fact that there is no difference in the effectiveness of alternating and direct current sparks when produced under similar conditions. Prof. Wheeler has informed the writer that he also has experimented with the two kinds of currents, and found no essential difference in the incendivity of the sparks produced by them.

Thornton's "Ionization" Test.

In a recent paper * Prof. Thornton has given an account of an experiment intended apparently to dispose of the thermal theory of ignition. His words are as follows :—

"The statement has been made here that ignition is electrical rather than thermal. As a test of this in the case of break sparks the following experiment was made. The least igniting current of a 35 per cent. hydrogen-in-air mixture was found by trial at 200 volts, 250 p.p.s. to be 0·4 ampere. The same poles were then sparked in pure hydrogen to remove oxide or occluded oxygen, and it was then found that the explosive mixture could not be ignited with less than 6 amperes broken. The sparks were large and bright but were electrically inert though their thermal value was many times greater than before. The first step in ignition is the formation of active oxygen ions. There is no difference between hydrogen and other gases except in sensitiveness to spark ignition."

It will be noticed that Prof. Thornton used alternating current for the production of his spark. Judging from the current values given he also used a non-inductive circuit. Seeing that the essential feature of the Thornton experiment lies in the "sparking" in pure hydrogen between the ignition experiments, the results should be independent of other factors. Consequently, in order to insure a high degree of precision, the author tried the experiment with a small air-core inductance in the circuit and used direct current.

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* "Researches on the safe use of electricity in Coal-mines," W. M. Thornton, Journ. Inst. Elect. Engin. vol. lxii. No. 330 (June 1924).

Experiments were repeated many times with hydrogen-air, methane-air, and coal gas-air mixtures, but in every case the current required for ignition was the same before and after sparking in hydrogen.

Experimental Irregularities.

It will be apparent that before the results of any ignition experiments can be admitted as having any theoretical value, the conditions under which the experiments are conducted must be rigorously investigated. The principal reason for this arises from the necessity for using $\frac{1}{2}Li^2$ or $\frac{1}{2}CV^2$, or one of the factors in those expressions, as a measure of the spark energy. In inductance spark experiments the quantity $\frac{1}{2}Li^2$ may give a figure differing greatly from the actual value of the energy imparted to the spark. Sometimes the figure is greater than the true figure, due, for example, to losses in the spark-producing system. Sometimes it is much less, due, for example, to extra, or unmeasured, energy being given to the spark from the current source, as when a high impressed voltage is used. In some experiments the inductive portion of the spark-producing system was varied. A coil was mounted, in the first instance, on one of the limbs of a laminated iron frame. When the current was adjusted to give an igniting spark, $\frac{1}{2}Li^2$ was equal to ·0023 joule. Then the same coil was mounted on a core in the form of a straight laminated iron bar. Under this condition ignition was obtained when $\frac{1}{2}Li^2$ was equal to ·0008 joule. Finally all iron was removed from the coil, giving an air-core, and the value of $\frac{1}{2}Li^2$ for ignition then became ·0006 joule. In all other particulars the experimental conditions were the same. Subsequent measurements, in a special calorimeter, of the heat actually dissipated in the sparks showed that the heat content of the sparks produced under the three different conditions was the same. The differences in the measured values of $\frac{1}{2}Li^2$ were due to core losses. Owing to the difficulty of standardizing an inductive system involving iron it is advisable to use air-core coils.

A well-known result in experiments with inductive sparks is that the energy required for ignition of a given gas (as measured by $\frac{1}{2}Li^2$) diminishes with increase of impressed voltage. The spark-producing system must include a source of electromotive force for supplying the requisite current. When the contacts are together, the voltage across them is practically zero. On separation the rise of voltage across the contacts depends not only on the inductive voltage, which first rises and afterwards falls, but also on the impressed voltage due to the source, which rises from zero to a maximum and persists. During the passage of the spark, energy is derived from both the stored magnetic energy of the system and the source, and the contribution from the latter, which may be large, is not included in the measurement of $\frac{1}{2}Li^2$. In one experiment using an air-core coil, for which $L = \cdot 0214$ henry, the current required to produce a spark capable of igniting an 8·5 per cent. methane-air mixture was ·77 amp. ($\frac{1}{2}Li^2 = \cdot 0063$), the voltage of the battery from which current was derived being 4 volts. Applying 220 volts to the system, the current required to produce an igniting spark, all other factors in the experiment being the same, was ·35 amp. ($\frac{1}{2}Li^2 = \cdot 0013$). Check experiments showed that the heat delivered to the spark was the same in the two cases, and the apparent difference of incendivity was due solely to the fact that the measure, $\frac{1}{2}Li^2$, does not take into account that contribution from the source which augments and tends to maintain the spark. In all work of a theoretical character on the incendivity of inductance sparks it is necessary to keep the impressed voltage as low as possible so that the energy derived directly from the source of current is negligible.

Capacity sparks, as already stated, are usually defined by the expression $\frac{1}{2}CV^2$. Here also difficulties are encountered. The charge given to the condenser is not wholly discharged across the spark-gap, although, under suitable conditions, the amount remaining in the condenser after the spark has passed is small and bears a definite relationship to the total charge. Using condensers with solid dielectrics, the residual charge may be relatively high, and what is worse, it is often irregular. In some experiments with glass condensers, the calibration curve giving the relationship between voltage and quantity of current discharged across the spark-gap showed well-marked steps. Mica and rubber were also found to be unsatisfactory. The most accurate results are obtained with air condensers, the charge remaining in the condenser after the spark has become extinct being small and regular.

Sparking voltage is a quantity which is often very erratic. When exposed to the open air of a room the sparking voltage of a given gap across which the voltage is raised gradually may be remarkably regular, but when contained in a small explosion chamber, voltages of as much as twice the normal break-down voltage have been observed before the spark occurred. It cannot be assumed, therefore, unless precautions are taken, that a spark-gap set to breakdown at a given voltage will always spark over at that voltage. With proper care, however, very great accuracy and consistency can be obtained when using capacity sparks ; in some experiments on methane, the difference in gap width necessary to convert a non-igniting into an igniting spark was within ·0005 inch. The above remarks apply to gradually applied voltages, and not to impulsively applied voltages such as are obtained when an ordinary induction-coil or magneto is used. Impulsively applied voltages are so liable to produce irregular and misleading results that they are hardly suitable for use in ignition research unless elaborate precautions are taken.

It is well-known that inductance sparks (or arcs) form more readily between some metals when separated than others. Wheeler has investigated this aspect of the subject, and finds that the energy required to produce a spark capable of igniting a given gas increases with the vaporization temperature of the metals used in the contacts. The proportion of the available energy which appears as heat in the spark diminishes with increase of vaporization temperature, consequently when a metal like platinum is used in the contacts, a larger current is required to give an igniting spark than when a metal like brass is used, other conditions in the circuit remaining the same. When sparks are produced between permanently separated electrodes (capacity sparks), the material of the electrodes appears to have no effect on the energy required to cause gas ignition.

It will be apparent from the foregoing that a necessary preliminary to any work on spark ignition is a thorough study of the experimental conditions, and until this is done no progress can be made in correlating the diverse results which are inevitably found when the experimental conditions are varied.

Summary.

The thermal theory of spark ignition asserts that ignition depends on the raising of a sufficient volume of the combustible gas to a sufficient temperature. It follows from a mathematical development of the theory that the energy required for ignition of a given gas varies with (*a*) the rate at which heat is imparted to the gas, and (*b*) the shape and proximity of the electrodes. The chief points of the present

paper may be summarized by stating the following experimental results which agree with the thermal theory of spark ignition :—

1. The incendivity of capacity sparks is found in general to be greater than that of inductance sparks, in accordance with the theoretical result that a source of short duration is more effective than one in which the heat is supplied over a longer interval.
2. The incendivity of capacity sparks depends upon the shape and relative position of the spark electrodes in a manner to be expected on the thermal theory.
3. The energy required for ignition of a given gas by low-voltage inductance sparks is constant over a wide range of values of self-inductance and current so long as the duration of the spark is constant.
4. There is no difference in the incendivity of inductance sparks produced in direct and alternating current circuits.
5. Experiments on the ignition of highly inflammable solids by means of very short hot wires show that the energy required for ignition increases with diminution of the rate of heating, and that over a wide range a linear relation exists between the energy and the time during which it is supplied.

It has also been shown in the paper that other important variations found in experiments are attributable to the manner in which the spark energy is measured.

XXXVI. *On a Critical Resistance for "Flashing" of Air Discharge-tubes.*

By JAMES TAYLOR, *B.Sc., Pemberton Fellow, and* WILLIAM CLARKSON, *M.Sc., Armstrong College, Newcastle-upon-Tyne*[*].

Abstract.

THE paper deals with a continuation of work on the "flashing" of discharge-tubes and the resistance relations necessary for the maintenance of "flashes." (For diagram of circuit see fig. 1.)

It is shown that there is a "critical" resistance R_c for the air discharge-tubes used, below which no flashing may be obtained, given by the relation

$$R_c = \frac{E - V_b'}{\psi(V_b')},$$

where E is the charging voltage, V_b' is the effective lower

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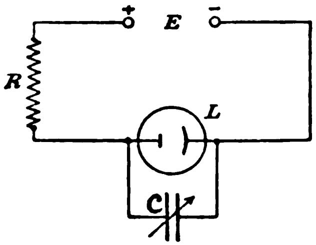
[*] Communicated by Prof. G. W. Todd, M.A., D.Sc.

critical voltage, and ψ (V_b') is the current voltage function, under the conditions of the experiments. A tentative explanation of the variation of the voltage intercept for the linear curves between the critical resistance R_c and the charging voltage E, with the capacity across the discharge-tube, is put forward.

Fig. 1.



E, the charging voltage.
R, the circuit resistance.
L, the discharge-tube.
C, the capacity shunted across the electrodes.

Introduction.

In a previous paper* the present writers showed, in the case of the neon discharge-tube or "Osglim" lamp, that there was a critical resistance below which the well-known phenomenon of "flashes" could not be obtained. The relation for this critical value is of the form

$$R_c = \frac{E - V_b}{k(V_b - V_a)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where E is the charging voltage, V_b is the lower critical voltage, V_a the cathode fall of potential approximately, and k the "conductance" of the lamp.

The above relation proceeded out of a simple theory of conduction in the discharge-tube, put forward by one of us in a previous paper †. The condition for no flashes is expressed physically by the fact that during any instant of the discharge through the tube, the quantity of electricity flowing from the condenser is exactly equal to the quantity which flows into the condenser from the charging battery.

In a recent paper on the study of "flashing" in air discharge-tubes some results were put forward tentatively in support of the relation of equation (1). The results were, however, neither definite nor conclusive, and a fuller investigation into the problem of the critical resistance of air discharge-tubes was proposed.

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* Taylor and Clarkson, Proc. Phys. Soc. Lond. xxxiv. pt. 4, p. 269.
† Taylor and Clarkson, Journ Scien. Instrs. i. No. 6, p. 174.

Some of the experimental difficulties underlying the investigation were pointed out. In the case of most tubes which are suitable for the investigation of the time relations of flashing, the conductivity is high and consequently the value of R_c is low. Fairly large currents are thus being carried by the tube at the critical resistances, and this makes for instability, due to the change of conductance and cathode fall with heating, and the intense bombardment of the electrodes by the ions. Furthermore, very serious difficulties are encountered, due to the presence of "salient" points * (described in another paper) which had the effect of increasing the conductivity of the tube and decreasing the value of the cathode fall of potential.

Very many types of tube were tried, including some with cooled electrodes, but the results were of a disappointing nature. The problem was to obtain a discharge-tube suitable for the production of flashes, but such that its conductance was sufficiently low to give values of R_c high enough to ensure repeatability and definiteness of results. The electrodes must furthermore be such that no salient points develop and no rapid change in the value of the cathode fall of potential should take place.

The tube most suitable for the experiments consisted of molybdenum or platinum wire electrodes, mounted in small glass stems, parallel to each other. The electrodes were fixed in a bulb of which the walls were sufficiently far removed from the electrodes to minimize "wall effects." The pressure was reduced and the tube "overrun" for several hours with the electrodes red-hot, due to the intense bombardment by the ions; the terminals were reversed from time to time so that each wire in turn was cathode. The tube was finally overrun for a considerable time in one direction. After overrunning in this way, most of the impurities had been removed from the electrodes, and they were in a fairly stable condition †. The tube was judged to be in a stable condition when the anode was covered with a uniform, thin, metal-like deposit, and the discharge spread itself uniformly over the electrodes. Notwithstanding this

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* Salient points are points at which small pieces of impurity (as alkaline salts from sealing-wax &c.) are situate. The presence of these "salient" points causes the discharge to be concentrated upon them, and completely alters the value of V_a from the normal.

† See also M. E. Dubois, *Comptes Rend.* clxxv. pp. 947–949.

treatment, the discharge-tube constants changed progressively with time and method of treatment, but to a much less extent than in the case of tubes which had not been overrun in this manner.

The preliminary experiments, taken over a wide range of pressures, showed that the E, R_c graphs were linear, but in the majority of cases intersected the voltage axis at an intercept different from the value V_b given by the theoretical relation of equation (1).

Since at the majority of pressures used the whole area of the cathode was employed during the luminous period, it was almost certain that the volt-ampere characteristics for the tubes were not of the linear form

$$i = k(V - V_a), \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which applied to the case of the neon discharge-tubes *.

Experiments carried out to check this have not, up to date, been very successful; the majority of the characteristics are, however, almost linear between the lower and upper critical voltages. It therefore became necessary to investigate theoretically the critical resistance function for any volt-ampere characteristic.

The Generalized Form of the Critical Resistance Function for the Discharge-tubes.

One of us (Taylor) has put forward the following generalized form for the critical resistances:—

If instead of a current-voltage function of the form of equations (2) or (6) we take a perfectly general one of the form

$$i = \psi(V), \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the condition for steadiness of the discharge is evidently

$$\frac{E-V}{R} \gtrless \psi(V) \quad .$$

$$\text{or} \qquad R \lessgtr \frac{E-V}{\psi(V)} . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If we assume, as is perfectly justifiable from experimental data, that $\psi(V)$ is a continuous function which increases with increase of V, we have evidently, if the range of possible values of V is from V_b' to V_c, that

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* Taylor and Clarkson, Journ. Scien. Instrs. i. No. 6, p. 174.

$$R_c = \frac{E - V_b'}{\psi(V_b')}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

where V_b' is the extinction voltage for the tube under the existing conditions.

Two cases are to be distinguished, viz.:—

(1) In which a portion only of the cathode is employed in carrying the discharge. Under these conditions the cathode fall of potential is constant and remains so until the whole of the cathode is covered by the negative glow.

(2) In which the full area of the cathode is employed during the discharge. Under these conditions an increase of the current density through the tube takes place concurrently with an increase of the voltage across the lamp terminals, and the cathode fall of potential attains values much in excess of the normal.

Under ideal conditions, with parallel plate electrodes, the linear characteristic would now be replaced by a relation of the form proposed by Aston,

$$V = FP^{-1}\sqrt{i} + G, \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

where F and G are constants, P is the pressure of the filling gas, V the voltage across the tube, and *i* the current.

In the tubes used in the present experiments, the full cathodic area was used continuously during the luminous period in flashing, and the work consequently comes under the second case.

The Variation of V_b *under different conditions.*

We should expect that if the value of the current through the tube be decreased suddenly, the magnitude of the cathode fall of potential would lag behind the normal value, which would be attained when the conditions become stable.

If V_b represents, as was suggested in a previous paper *, the cathode fall of potential plus a voltage just sufficient to carry the ions over to the anode, then the instantaneous value of the lower critical voltage V_b' will now be greater than the normal value V_b.

The simple relation of equation (1) for the critical resistance will now be replaced by the more comprehensive one of equation (5). Now it is to be expected that under given conditions, with a fixed value of the capacity across the electrodes so that a constant quantity of electricity is thrown through the lamp during every luminous period, the function of $\psi(V_b')$ will also be constant, and the above relation will be linear. The intercept of the E, R_c graphs with the voltage axis will, however, vary from the normal value V_b by the divergence of V_b' from that value.

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* Taylor and Clarkson, Journ. Scien. Instrs. i. No. 6, p. 174.

It is to be expected that V_b' will depend upon the value of the capacity C across the discharge-tube terminals, upon the rapidity with which the changes are effected, the nature and condition of the electrodes, and the gas-pressure.

Furthermore, it is reasonable to suppose that there will be a greater lag with currents of high value at the beginning of the luminous period than with currents of smaller initial value. The current at the beginning of the luminous period is, of course, a function of the upper critical voltage V_c, and will evidently—for a given discharge-tube—be greater the greater the value of V_c. It is therefore necessary to ascertain whether there is any variation of V_c with the value of the capacity C.

The Variation of V_c *with the Capacity* C.

The variation of V_c may be considerable. V_c has a higher value initially than when the discharge has *just ceased*, and is furthermore somewhat lower when rapid flashes are taking place through the tube, owing presumably to the persistence of the space-charge round the cathode [*].

Indeed, when the value of the capacity across the discharge-tube electrodes is such as to give (when a telephone is included in the circuit) notes of audible frequency, the note or flashing may be maintained, provided the discharge is once initiated at values of E, the charging voltage, considerably below the normal value of V_c, the upper critical voltage.

From the above facts it may be concluded that the value of the current through the discharge-tube is greater when large capacities are used than in the case of small capacities. This is supported experimentally by the fact that the flashes are much brighter for large than for moderately small capacities. Consequently a greater lag and variation of the going-out voltage from the normal is to be expected in the case of large capacities than in the case of the small ones.

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[*] The authors are aware that the time for the space-charge to establish or disestablish itself is of the order of 10^{-6} sec. in a pure gas. But it is to be observed that when very rapid flashes are taking place, the current will never be of zero value at any instant of the extremely short "dark" period, for there is the ordinary Townshend current, due to the ionization by collision from the residual ions, which finally builds up into the glow discharge (*e.g.* see E. Reiche, *Ann. der Physik*, F. 4, B. 52, 1917). Persistence of the space-charge is used here simply to indicate the presence of residual ionization in the gas, which is the usually accepted explanation of the variation of the "sparking" potentials in gases.

When very small capacities are used (about 0·004 microfarad and less) the flashes are of very feeble brightness; the extinction voltage it is to be expected, therefore, will differ little, if at all, from the normal value.

The Variation of the Current Function $\psi(V_b')$ *with Capacity.*

In a general way it is to be expected, since the energy transferred across the tube in the luminous period decreases with decrease of the capacity across the electrodes, that the current function will decrease with C as the energy transference becomes less. Considering equation (5),

$$R_c = \frac{E - V_b'}{\psi(V_b')},$$

since V_b' decreases as the capacity C becomes less, R_c will increase with decrease of C. Now the variation of V_b' is not in most experiments of a great order, for, as will be shown later, the E, R_c graphs do not intercept the axis of voltage at points very far removed from the normal lower critical voltage V_b; consequently R_c may be expected to increase slowly with diminution of C.

This is what actually happens in practice (see the graphs of fig. 6) down to capacities of about 0·004 microfarad; from this point, however, the critical resistance function begins to increase rapidly, due presumably to the very small energy transference possible during the luminous period. This, of course, makes the effective resistance of the tube high, and correspondingly decreases the value of the current function $\psi(V_b')$.

THE EXPERIMENTAL RELATIONS.

The Critical Resistance Relations for Large Capacities of the order of 1 *microfarad.*

Tables I. and II. and the graphs of figs. 2 and 3 show the results obtained in the case of a capacity of approximately 1 microfarad for the E, R_c functions over a wide range of pressures.

TABLE I.

Molybdenum-wire electrode discharge-tube.

Length of electrodes = 3·4 cm. Distance apart = 0·8 cm.

No.	P. Pressure. in mm.	V_b'. Intercept.	V_b. mean.	i_c. microamps. mean.	Slope of graph.	Diam. —glow. cm.	Anode glow.
(1)...	4·06	350	315	1170	1090	0·25	Little at top of electrode.
(2)...	3·28	306	310	935	949	0·275	Do.
(3)...	2·68	350	317	982	875	0·4	Faint on part of electrode.
(4) ..	2·4	290	315	984	750	0·45	Do.
(5)...	2·16	380	315	987	733	0·55	Glow.
(6)...	1·74	315	314	618	595	0·6	Even glow.
(7)...	1·46–1·49	315	307	518	503	0·7	Do.
(8)...	1·22	302	299	436	433	0·775	None.
(9)...	1·01	300	292	330	324	0·9	None.
(10)...	0·87	280	290	278	290	1·15	None.
(11)...	0·86	275	292	252	265	1·15	None.
(12)...	0·75	270	292	198	210	1·4	None.
(13)...	0·65	285	293	167	174	1·5	None.

Value of Capacity across the tube terminals = 0·977 microfarad.

Fig. 2.—Graphs showing the Relationship between the Charging Voltage E and the Critical Resistance R_c for a Capacity of 1 microfarad, at various Pressures.

Molybdenum-wire electrode discharge-tube.

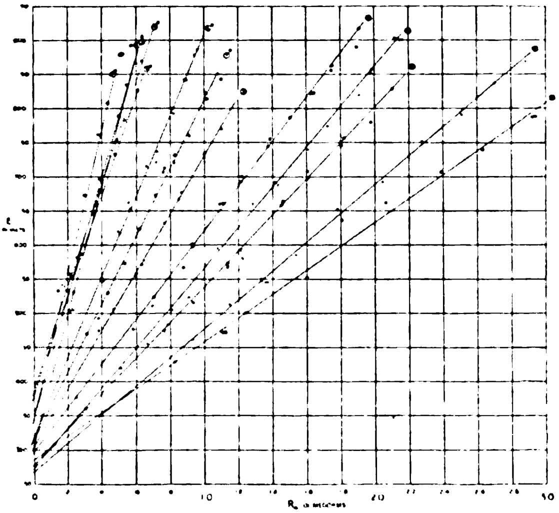


TABLE II.

Platinum-wire electrode discharge-tube.

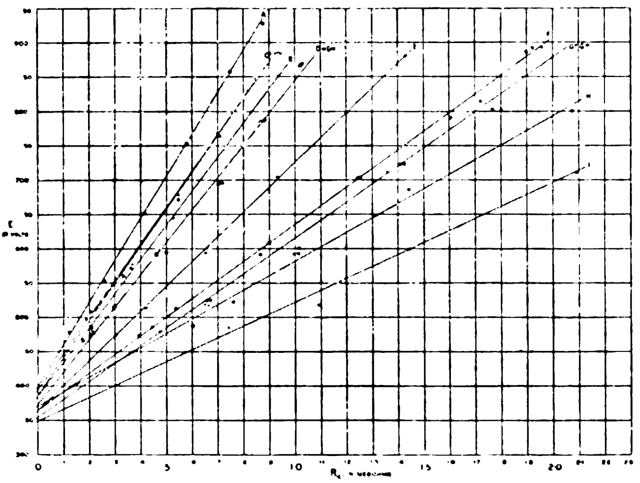
Length of electrodes =2·5 cm. Distance apart =0·65 cm.

No.	P. Pressure in. mm.	V_b'. Intercept.	V_b. mean.	i_b. microamps. mean.	Slope of graph.	Diam. —glow. cm.	Anode glow.
(A) ...	2·58	400	382	614	612	0·45	Almost full electrode; bright.
(B) ...	2·18	385	382	499	498	0·5	Do.
(C) ...	2·17	394	368	573	528	0·45	Glow.
(C′) ...		388		569	534	Do.	Do.
(D) ...	1·87	373	373	490	474	0·55	Do.
(D′) ...	Do.	Do.	372	490	Do.	Do.	Do.
(E) ...	1·43	365	366	363	363	0·75	Do.
(F) ...	1·175	365	366	275	270	0·85	All. Velvety.
(G) ...	1·04	355	368	246	261	0·95	Do.
(G′) ...				253			
(H) ...	0·94	370	370	215	211	?	?
(I) ...	0·82	348	368	165	174	Fills inter-space.	Full.

Value of Capacity across the tube terminals =0·977 microfarad.

Fig. 3.—Graphs showing the Relationship between the Charging Voltage E and the Critical Resistance R_c for a Capacity of 1 microfarad, at various Pressures.

Platinum-wire electrode discharge-tube.



The tube used in the experiments of which the data are given in Table I., was a molybdenum wire electrode discharge-tube, and that for Table II. a platinum wire electrode tube. The dimensions of both tubes are recorded in the tables.

Unfortunately it was not found possible to investigate the variation of R_c with capacity when the latter was more than about 1 microfarad, owing to the lack of suitable capacities. The upper critical voltage for these tubes is between four and five hundred volts, and the condensers used must, of course, be able to withstand this voltage without leakage, or the results are unreliable. It was found, however, that so far as could be ascertained, the variation of R_c was not more than a few per cent for capacities of from 0·5 to 4 microfarads.

A few general remarks relative to the experimental results may be introduced. When a tube which has been overrun is employed, it is found to be in a fairly stable condition; but notwithstanding, progressive variations of the constants of the tube occur, and the lower critical voltage especially is subject to variations.

If a tube is run for a considerable time at the critical resistance, there is a general tendency for the value of this latter to decrease; for the heating and "fatigue" effects result in an increase of V_a the cathode fall of potential (consequently increase of V_b), and increase of the conductance of the lamp *.

As will be seen from equations (1) and (5), these changes result in a decrease of R_c, the critical resistance. When, however, the tube has settled down to the particular conditions, the variations of R_c are not very grave.

A consideration of Tables I. and II. and the graphs of figs. 2 and 3 for the two discharge-tubes gives rise to the following general results:—

(1) The critical resistance functions are, for all the experimental pressures, linear within the limits of experimental error.

(2)

(*a*) In the case of the platinum-wire tube, the graphs of pressures 2·58, 2·17 mm. [(A), (*c*), and (*c*′)] definitely intercept the voltage axis at a value greater than V_b, the lower critical voltage. The graph of 2·18 mm. (B), however, intercepts at V_b.

(*b*) In the case of the molybdenum-wire discharge-tube, the graphs of pressures 4·06, 2·68, 2·4, 2·16 mm. [(1), (3), (4), and (5)] definitely intercept at a value greater than V_b.

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* *Cf.* Schaufelberger, *Ann. der Phys.* (4), lxxiii. No. ½ (1924).

(3)

(*a*) The graphs of pressures 2·18, 1·87, 1·43, 1·175, 0·94 mm. [(B), (D), (E), (F), and (H)] intercept at the value V_b.

(*b*) The graphs of pressures 3·28, 1·74, 1·22, 1·01 mm. [(2), (6), (8), and (9)] intercept at V_b; graph (7) of pressure 1·46 to 1·49 intercepts at a value rather greater than V_b, but there was a slight leak in the apparatus in this case.

(4)

(*a*) The graphs of pressures 1·04, 0·82 mm. [(G), (I)] have intercepts less than V_b.

(*b*) The graphs of pressures 0·86, 0·87, 0·75, 0·65 mm. [(11), (10), (12), and (13)] intercept at values less than V_b.

(5) On the average, where the intercept is greater than V_b, the slope of the critical resistance graph is less in value than the current reading R_c.

Where the voltage intercept is of the value V_b, the slope of the graph is of the same value as the current at the critical resistance.

Finally, where the voltage intercept is less than V_b, the slope of the graph is less in value than the current at R_c.

Considering the equation (5), we see that the current at the end of the flash, just before the discontinuous change from "flashing" to steady conditions, is given by

$$i' = \frac{E - V_b'}{R_c},$$

and when the conditions have become steady, the current is given by

$$i = \frac{E - V_b}{R},$$

so that evidently $i' < i$ if $V_b' > V_b$; that is to say, the slope of the E, R_c graphs, $\frac{dE}{dR_c} = \psi(V_b') = i'$, is less than the steady current at the critical resistance.

Further, we have $i' = i$ if $V_b' = V_b$, and the slope of the graph will be of the same value as the steady current at R_c; and finally, if $V_b' < V_b$, $i' > i$, and the slope of the graph is of greater value than the current at the critical resistance.

It is at once evident that the foregoing experimental results agree substantially with the predictions based upon the above considerations of the critical resistance function of equation (5).

(6) It is noticeable, from a consideration of the tables, that, in a general way, at the higher pressures used, about 2 mm. and above, the voltage intercept is greater than V_b; at the medium pressures, 1 to 2 mm. (approx.), the intercept is of the value V_b; and at lower pressures, on the average, the intercept is less than the lower critical voltage V_b.

The experiments were, of necessity, not carried out all in one day for the different pressures, and this partly accounts for the changes in the discharge-tube constants, where the pressure is approximately the same. The sole large variation is found in the case of (C) and (C′) in Table II. for the platinum electrode tube. These results were taken prior to the others, on a different day, and diverge from those of (B). The value of V_b is usually lower, however, initially, than the final value attained after the tube has settled down to the working conditions.

Note on the Pressure-range over which "Flashes" may be obtained.

In the case of the platinum wire electrode discharge-tube, flashing was obtained down to a pressure of 0·07 mm., with a charging voltage of approximately 950 volts. The negative glow under these circumstances was very diffuse, and almost filled the bulb of the discharge-tube.

There does not appear to be any definite upper limit to the pressure at which flashes may be obtained, apart from the limit imposed by the voltage available.

The Critical Resistance Relations for Small Capacities, of the order of 10^{-1} *microfarad.*

A series of the E, R_c graphs were taken, over a range of pressures, for small capacities of the order of 10^{-1} microfarad.

Table III. and the graphs of fig. 4 give the results in the case of the molybdenum-wire electrode discharge-tube for a capacity of 0·016 microfarad, over a range of pressures; Table IV. and the graphs of fig. 5 give the similar results for a capacity of 0·00875 microfarad.

A consideration of the tables and the graphs gives, as in the case of the larger capacities, the following general results:—

(1) The functions are all, within the limits of experimental error, linear.

(2) All the voltage intercepts of the graphs are of greater value than the lower critical voltage V_b, except in the case of graph IV. of Table IV., where the intercept is equal to V_b.

TABLE III.

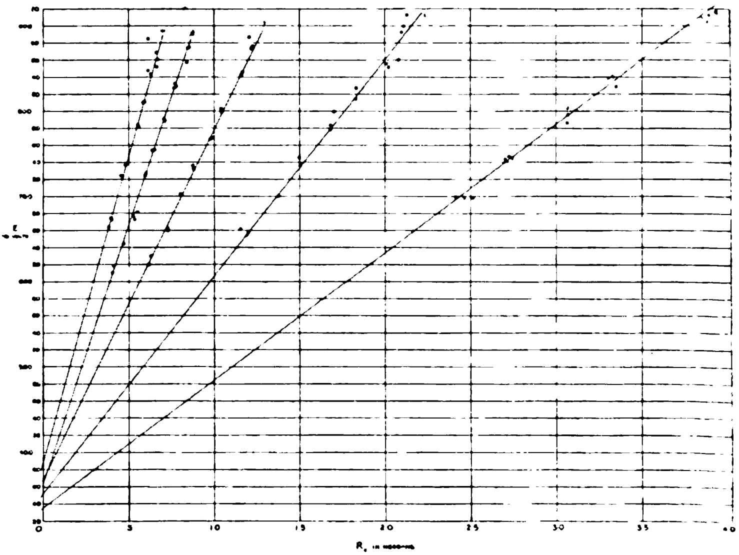
Molybdenum-wire electrode discharge-tube.

No.	P. Pressure in mm.	V_b'. Intercept.	V_b. mean.	i_c. micro-amps. mean.	Slope of graph.	V_e, av. voltage before current becomes steady. mean.
(α)......	2·52	390	349	816	710	408
(β)......	2·0	360	345	652	603	396
(γ)......	1·49	350	333	450	430	380
(δ)	1·08	347	329	282	258	?
(ε)......	0·67	336	330	164	150	?

Value of Capacity across the tube terminals =0·016 microfarad.

Fig. 4.—Graphs showing the Relationship between the Charging Voltage E and the Critical Resistance R_c for a Capacity of 0·016 microfarad, at various Pressures.

Molybdenum-wire electrode discharge-tube.



The intercept has in all cases a value between V_b, the lower critical voltage, and V_e, the average voltage across the tube terminals just before steadiness of the discharge ensues (see later, in section on the variation of R_c, V_b, etc. with C), and approaches nearer to the value V_b as the pressure is reduced.

TABLE IV.

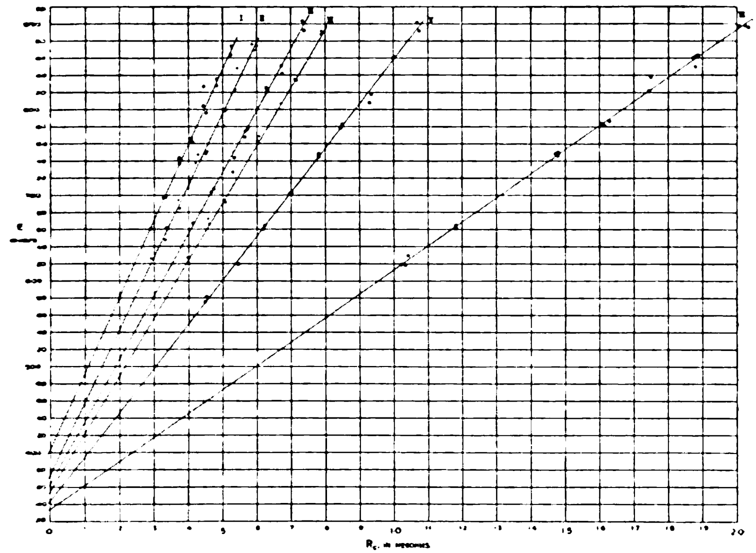
Molybdenum-wire electrode discharge-tube.

No.	P. Pressure. in mm.	V_b'. Intercept.	V_b. mean.	i_c. micro-amps. mean.	Slope of graph.	V_e, av. voltage before current becomes steady. mean.
(I.)...	3·14	402	348	1032	888	414
(II.)...	2·75	374	357	886	842	410
(III.)...	2·37	363	346	752	726	400
(IV.)...	2·10	354	354	676	675	395
(V.)...	1·62	344	331	528	514	374
(VI.)...	1·09	334	322	289	280	365

Value of Capacity across tube terminals $=0·00875$ microfarad.

Fig. 5.—Graphs showing the Relationship between the Charging Voltage and the Critical Resistance R_c for a Capacity of 0·0085 microfarad, at various Pressures.

Molybdenum-wire electrode discharge-tube.



(3) Where the voltage intercept of the graph is greater than V_b, as is to be expected, the slope of the graph $\left(\frac{dE}{dR_c}\right)$ is less in value than the steady current reading at the critical resistance R_c.

In the case of graph IV. of fig. 5, where V_b', the voltage intercept, is equal to V_b, i' the slope of the graph is equal in value to i the current at the critical resistance.

It will be noticed that there has been a considerable change in the value of V_b, between the obtaining of the results for the 1 microfarad capacity, and the above results.

The Variation of R_c, V_b, *etc. with* C.

The variation of the critical resistance R_c with the capacity was investigated at two different pressures for the molybdenum-wire electrode discharge-tube. Table V. and the graphs of fig. 6 show the variations.

With large capacities the critical resistance increased gradually with diminution of C, but when the capacity became of the order of 0·004 microfarad and less, the value of R_c began to increase rapidly with decrease of C, and in the case where the voltmeter alone was across the lamp terminals, attained several times the value for large capacities.

The voltage across the lamp electrodes at the point where the discharge changes discontinuously from the flashing to the steady state was observed together with the current, as given by a unipivotal galvanometer, for this critical point. As the discharge under these conditions is periodic in character, it is apparent that the voltage reading V_e is the average voltage over the complete cycle of the condenser charging and discharging between the upper and lower critical voltages. These measurements are given in Table V.

It is noticeable that when the circuit resistance is somewhat greater than the critical resistance value, the voltage across the lamp terminals, when small capacities are used, remains constant for a considerable range of resistance as R is decreased. We would conclude from this constancy that V_e represents the limiting average voltage over the whole cycle, when the luminous period becomes great in comparison with the "dark" period.

The practically obtained value is not sufficiently constant to compare directly with that derived theoretically; moreover, the variations of V_b and V_c with C inhibit any comparison based on the normal values of these voltages.

V_e, as is to be expected, decreases with decrease of C, for both V_c and V_b become less in magnitude, and consequently the average voltage over the whole cycle between V_c and V_b (that is V_e) will decrease with decrease of the capacity.

The current reading i_e is similarly the average current over the total period, whilst i, given in Table V., is the current value when the discharge becomes truly steady.

TABLE V.

C. microfarads.	V_e mean.	V_b. mean.	R_c. mean.	*i* . microamps. mean.	*i*. microamps. mean.
0·977	—	314	0·47	—	541
0·063	380	316	0·53	336	475
0·055	377	316	0·535	334	469
0·066	375	316	0·56	323	456
0·031	377	317	0·565	306	445
0·016	372	314	0·57	348	448
0·0088	367	316	0·57	350	446
0·0041	357	317	0·595	352	426
0·0023	329	317	0·63	338	402
0·0012	332	316	0·69	314	351
0·0004	326	315	0·89	240	274
0·00007 Voltmeter alone.	324	315	1·13	198	208

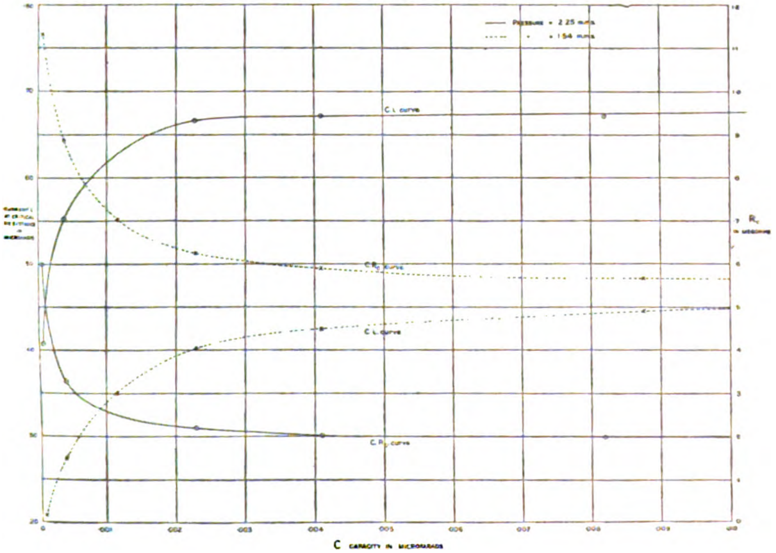
Pressure of air in tube =1·45 mm.

C. microfarads.	V_e mean.	V_b. mean.	R_c. mean.	*i* . microamps. mean.	*i*. microamps. mean.
0·977	—	326	0·978	—	832
0·055	414?	327	0·13	528	752
0·032	395·5	327	0·153	568	716
0·015	386	328	0·182	564	694
0·0082	383	324	0·202	556	672
0·0041	382	326	0·207	568	674
0·0023	376	327	0·223	580	668
0·0004	362	328	0·33	510	554
0·00007 Voltmeter alone.	348	325·5	0·6	356	408

Pressure of air in tube =2·25 mm.

Fig. 6.—Graphs showing the Variation of the Critical Resistance R_c with the Capacity C for two different Pressures.

Molybdenum-wire electrode discharge-tube.



Both i_e and i decrease with decrease of the capacity across the lamp electrodes. With large capacities the diminution with C is very slow down to a point at a capacity of about 0·004 microfarad (the same point at which R_c begins to increase rapidly), where a very rapid diminution of these quantities, as C is made less, sets in.

When the discharge has attained a steady state, the tube of course adjusts itself to carry the maximum current possible under the existing conditions—that is, the voltage across the lamp terminals drops to the lowest possible value, V_b. This voltage as well as the current i was measured. V_b, as is shown in the table, is found within the limits of experimental error to be independent of the capacity C.

The Variation of the Effective Lower Critical Voltage V_b'.

It has been shown in the case of the "Osglim" lamp that the going-out or extinction voltage (lower critical voltage) is of greater value than normal when *sudden reduction* of the current in the circuit is made by reduction of the voltage across the lamp terminals *. The present authors have observed a similar phenomenon in the air discharge-tubes used in these experiments. Mr. Tarrant, in his contribution to the discussion on a previous paper on the critical resistances for the "Osglim" lamps, states that the lower critical voltage for the lamp is not constant if large charges are passed through the lamp during the luminous period †. "Under these conditions the extinction voltage for the lamp was considerably higher than that measured when the lamp was running in a steady state, or when a small parallel capacity only was used" ‡.

One of us, in recent preliminary experiments on the variation of the lower critical voltage with the capacity across the lamp and the energy thrown through during the luminous period, has observed similar variations, though not so great as those observed by Mr. Tarrant (the lamps were aged by overrunning). It appears that similar results hold in the case of the air discharge-tube.

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* Shaxby and Evans, Proc. Phys. Soc. Lond. xxxiv. pt. 4, p. 280.

† It may be pointed out here that in the experiments on the critical resistance of the "Osglim" lamps, previously referred to, the conditions were such (since resistances were included in the condenser circuit so that a part only of the cathode was employed in discharge, and variations were made gradually) that V_b' corresponded, within the limits of experimental error, to the normal lower critical voltage V_b.

‡ See Proc. Phys. Soc. Lond. xxxiv. pt. 4. Discussion (Mr. A. G. Tarrant), p. 280.

The experimental results are then, at least qualitatively, in agreement with those predicted in the theoretical section of the present paper. They certainly confirm the fact of the divergence of the effective lower critical voltage V_b' from the normal V_b, in the case of the 1 microfarad capacity, at pressures above 2 mm., and in the case of the small capacities over a much wider range. Unfortunately, the results obtained above, for the divergence of V_b' from V_b, do not lend themselves to any quantitative codification. In a general way it has been demonstrated, by taking graphs for many small capacities, that the voltage intercept, in agreement with the deductions made in the theoretical section on the variation of V_b', approaches nearer to the normal value V_b as the capacity across the lamp is made less. The results obtained are not sufficiently consistent for the authors to make any final claims in the matter.

Certain results seem to indicate that the erratic values obtained for V_b', even at the same pressure, may be intimately connected with the appearance and disappearance of the anode glow.

Experiments carried out to determine whether there was any connexion between the types of the discharge and the values of V_b' were inconclusive. The sole general rule that is apparent is for the tubes with large capacities across them. Where there is an anode glow, the value of V_b' is either greater than or equal to that of V_b, and where there is no anode glow, V_b' is either less than or equal to V_b.

In conclusion, we wish to acknowledge our indebtedness to Prof. G. W. Todd, of Armstrong College, under whose supervision the experiments were carried out, and to the Department of Scientific and Industrial Research for the grant which has enabled one of us to undertake the work.

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XXXVII. *Chemical Affinity and Electronic Structure.—Part I. The Non-polar Bond.* *By* BERNARD HOWELL WILSDON [*].

THE recent great advances in our knowledge of the constitution of the atom have resulted in various attempts to construct a theory which will explain the main facts of chemistry included under the name affinity. So far, these have been of only a qualitative or descriptive nature. While they enable systems of chemical notation, more or less complicated, to be expressed in terms of electrons, which may aid the chemist in visualizing the chemical bond, it is scarcely to be expected that they will afford a basis for a quantitative theory unless the mechanism postulated corresponds with physical realities. For this reason a static model molecule, such as that associated with the names of Lewis and Langmuir, cannot long meet all the requirements of a theory of chemical combination.

In what follows is given an outline of a theory which it is believed will at least provide a basis for the discussion of chemical combination in a manner consistent with our present knowledge of the atom. It has the further merit of being quantitative; besides affording a method of attacking the energetics of reactions, it also gives some insight into the geometrical structure of the molecule.

The fundamental assumption on which the theory rests is that, in order that the free valency orbits of uncombined atoms shall be capable of forming a chemical link or bond, they must have identical or harmonically related frequencies (see Note at end of paper). Change in the frequency of an electronic orbit, without a jump of the principal quantum number, may be brought about either by the precessional rotations which result from the action of a magnetic field, or by the nutational movements impressed by an electrostatic field. Conversely, we may legitimately regard a change in the natural frequency of an orbit which takes place without the large energy change involved in a jump of the principal quantum number, as *producing* a magnetic or electrostatic field. The accommodation in frequency which we assume to be necessary in order that two discordant orbits shall unite to form a chemical bond, may therefore be supposed to be quantitatively related to the field of force which binds two atoms. Bonding brought about by a magnetic field will obviously correspond with a non-polar type of combination; an electrostatic origin will then give rise to the polar bond.

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[*] Communicated by Dr. J. W. Nicholson, F.R.S.

A change in frequency of an orbit represents only a change in kinetic energy. Associated with this there will be a change in potential energy. In the case of an electrostatic field it is known that the kinetic energy of an orbital electron bears always a constant ratio to the potential energy. This result was due originally to Bohr (Phil. Mag. xxvi. p. 24, 1913), who states: "In every system of nuclei at rest and electrons which move in circles with velocities which are small compared with the velocity of light, the kinetic energy except in sign, is equal to half the potential energy." Sommerfeld (*cf.* 'Spectral Lines and Atomic Structure,' Eng. Trans. p. 447) has generalized this theorem, which he shows is not limited to circular orbits when time mean values are considered. The Coulomb field may also be replaced by any other in which a definite law of force holds. Under these conditions it is shown that if the potential energy of the field is a homogeneous function of degree $n+1$ of the coordinates of position, in general, the time mean values of the kinetic and potential energies will be related as follows:

$$E_{\text{kin.}} = \frac{n+1}{2} E_{\text{pot.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the case of a non-polar bond, since the magnetic moments of the orbits are quantized, we may represent dimensionally the work done in breaking the bond by an equation of the form

$$-W = \frac{\Sigma\mu_1\mu_2}{r^3},$$

where $\Sigma\mu_1\mu_2$ represents the scalar product of the magnetic moments and r is some linear coordinate. The law of force will therefore be given by

$$\frac{\partial W}{\partial r} = F = \frac{3\Sigma\mu_1\mu_2}{r^4},$$

whence n in equation (1) is equal to -4; substituting in (1) we have

$$E_{\text{kin.}} = -\tfrac{3}{2} E_{\text{pot.}};$$

consequently

$$Q = \Delta E_{\text{kin.}} + \Delta E_{\text{pot.}} = \tfrac{1}{3}\Delta E_{\text{kin.}}, \quad . \quad . \quad . \quad (2)$$

where Q is the total energy change.

As our assumption regarding the tuning of free orbital frequencies enables us to estimate the change in kinetic energy from a knowledge of the natural frequencies of the orbits of uncombined atoms, it should be possible, under conditions which will be described later, to make use of the above relation between the kinetic and potential energies of orbits in a magnetic field to calculate the heats of formation of non-polar compounds. It will be shown below that heats of formation can be calculated which agree well with those observed for simple compounds, using only theoretical values for the frequencies of atoms in their ground orbits and without the use of arbitrary quantum numbers.

The available energy of bond formation.—When similar atoms combine, if both valency electrons are in their ground orbits, their frequencies will be the same and there will consequently be no energy available by accommodation in frequency, to provide the energy of the bond. This is not the case in the union of dissimilar atoms: here, the accommodation in the frequencies of the naturally discordant ground orbits is capable of providing the bond energy. We may infer, therefore, that it is only in the combination of similar atoms that activation is a necessary preliminary to reaction. This does not of course preclude the possibility that activation may also occur in other types of combination.

The energy of activation does not enter into the balance sheet which represents an ordinary thermochemical reaction: otherwise, the reaction which takes place when hydrogen atoms combine to form the hydrogen molecule should be endothermic, which is not the case. On decomposition of such a molecule the energy required will be that necessary to re-form one activated and one unactivated atom. If the activated atom then resumes its ground orbit the light quantum emitted will not be recorded as a heat change.

We therefore suppose the energy available for bond formation is given by

$$h(\nu_1-\nu_2), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ν_1 and ν_2 represent, either the natural frequencies of two dissimilar atoms, or the frequencies of similar atoms at two different energy levels. The difference of the two terms then corresponds with the energy of emission of a spectral line. In what follows, the natural frequencies ν_1 and ν_2 are calculated from the formula

$$\nu = \mathrm{R}_0\frac{Z_e^2}{n^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Here R_0 is the Rydberg constant, Z_e is the effective atomic number and is equal to the number of electrons in the valency shell minus the screening number of Sommerfeld; n is the principal quantum number of the orbit. Values for s_p, the screening number, and Z_e^2 for different numbers of valency electrons p, are given for reference in Table I. These numbers correspond with vertical columns of the periodic table of the same number as p.

TABLE I.

p.	s_p.	Z_e^2.
1	0·000	1·000
2	0·250	3·061
3	0·577	5·862
4	0·957	9·249
5	1·377	13·13
6	1·828	17·40
7	2·305	22·05

From (4), if E_a represents the available bond energy per gram molecule, we have

$$E_a = \frac{hR_0}{J} L\left(\frac{Z_{e_1}^2}{n_1^2} - \frac{Z_{e_2}^2}{n_2^2}\right), \quad . \quad . \quad . \quad . \quad (5)$$

where L is Avogadro's number and J is the mechanical equivalent of heat. The factor, $A = \frac{hR_0}{J}$, becomes on substituting the values, $R=109721{\cdot}6$ sec.$^{-1}$, $h=6{\cdot}55\times10^{-27}$ erg secs., $L=0{\cdot}606\times10^{24}$, and $J=4{\cdot}187\times10^{7}$ erg/cal.,

$A = 310{\cdot}2$ kilogram calories per gram molecule.

Calculation of the change in kinetic energy on bond formation.—E_a, the available bond energy, will only represent the change in kinetic energy on combination under certain conditions. If energy is used in distorting the constituent elements of structure of the molecule, the change in kinetic energy must necessarily be less than the available energy calculated from (5). The distribution of energy in the molecule may then be expected to correspond with what takes place in the anomalous Zeeman effect in the magnetic resolution of spectral lines. The change in kinetic energy will thus be affected by a factor similar to the Runge denominator. The normal or Lorentz resolution, represented by $\Delta\nu_{\text{norm.}}$, only occurs when the impulse taken up by the electronic orbits does not affect other orbits or the molecular trunk. It is, however, this "normal resolution" representing purely kinetic energy which it is our object to calculate. If all the available bond energy were retained in kinetic form in the molecule, $h\Delta\nu_{\text{norm.}}=E_a$ would give the work which would be done in restoring the original frequencies of the electronic orbits in each atom, *i.e.* the Runge denominator is equal to unity. By (2) one-third of this amount would represent the total energy change and would thus give the heat of decomposition of the molecule.

In order to calculate the distribution of the available bond energy in the molecule, we may make assumptions similar to those of Landé (*Zeitschr. f. Phys.* 1921, p. 231) in the calculation of the anomalous Zeeman effect. The hypothesis is adopted that the distribution of impulse depends on changes by half units in the azimuthal quantum numbers of the orbits. The impulses corresponding with these changes may affect both electronic orbits and molecular trunk. We may calculate the energy of the molecule on the supposition that the orbits in one half are affected by an external magnetic field originating from the second half. By symmetry the total energy will then be given by twice this amount, since the action of both halves of the molecule must be reciprocal. Following the method of spatial quantizing developed by Sommerfeld, we may also assume that besides the quantum restriction to changes in the moments of orbits, connected with change in their azimuthal quantum numbers, also their components in the molecular field can only attain discrete values. This assumption gives a relation determining the orientation of orbits in the molecule.

In the simplest cases, where the trunk is incapable of acquiring magnetic moment, or where the impulses to which it is subjected are of opposite sign, the whole available energy of the bond will be confined to the interaction between orbits and field. If k represents the azimuthal quantum number of the free valency orbit, we assume that it changes, under the influence of the field of the second atom, to $k-\frac{1}{2}$. If the trunk remains unaffected, the energy of the orbit in the field of the second atom will be given by

$$(k-\tfrac{1}{2})\mathrm{BH}\cos\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where B is the unit of magnetic moment of Bohr, and is equal to $eh/4\pi mc$, e being the charge of an electron, h the Planck unit of action, m the mass of the electron, and c the velocity of light. H is the field strength of the second atom, and θ the angle made by the vector normal to the orbit with the direction of H. Lorentz's equation for the normal resolution of spectral lines in a magnetic field is

$$\Delta\nu_{\text{norm.}} = \frac{e\text{H}}{4\pi mc} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Substituting in (6) we have, including the symmetry factor 2,

$$\text{E}_a = 2[(k-\tfrac{1}{2})\cos\theta]h\Delta\nu_{\text{norm.}}, \quad . \quad . \quad . \quad (8)$$

The possible values of $\cos\theta$ are given by combinations of $\frac{l_1}{l_1+l_2}$, where l_1 and l_2 are Sommerfeld's equatorial and latitudinal quantum numbers whose sum l_1+l_2 (usually denoted by n_1+n_2) is equal to k the azimuthal quantum number.

In the case of hydrogen where k changes to $(1-\frac{1}{2})$ the only possible values of $\cos\theta$ are 0 and 1. $\cos\theta$ must therefore be equal to 1, *i.e.* the orbit adjusts itself at right angles to the direction of the field of the second atom. Substituting for E from (5) we have

$$\text{E}_a = \text{A}\left(\frac{\text{Z}_{e_1}{}^2}{n_1{}^2} - \frac{\text{Z}_{e_2}{}^2}{n_2{}^2}\right) = 2(k-\tfrac{1}{2})\cos\theta \, . \, h\Delta\nu_{\text{norm.}},$$

whence

$$\Delta\nu_{\text{norm.}} = \text{A}\left(\frac{\text{Z}_{e_1}{}^2}{n_1{}^2} - \frac{\text{Z}_{e_2}{}^2}{n_2{}^2}\right) \cdot \frac{1}{2(k-\frac{1}{2})\cos\theta} \cdot$$

Q will then be given by

$$\text{Q} = \tfrac{1}{3}h\Delta\nu_{\text{norm.}} = \frac{\text{A}}{3}\left(\frac{\text{Z}_{e_1}{}^2}{n_1{}^2} - \frac{\text{Z}_{e_2}{}^2}{n_2{}^2}\right) \cdot \frac{1}{2(k-\frac{1}{2})\cos\theta} \cdot \quad (9)$$

For the hydrogen molecule we thus obtain, since $\text{Z}_e{}^2 = 1$, $n_1 = 1$, $n_2 = 2$, $\cos\theta = 1$,

$$\text{Q} = \frac{310 \cdot 2}{3}\left[\frac{1}{1} - \frac{1}{4}\right] \cdot \frac{1}{1} = 77 \cdot 55 \text{ Cal.}$$

This compares favourably with the experimental value of 85 calculated by Langmuir and the value of 81 found by Frank and Knipping (*Ber. Deut. Phys. Gesch.* xxi. p. 738, 1919). The calculated value is within the probable experimental value of the determinations.

With the halogen elements the outer valency electron has a value of $k=2$, which changes to $(2-\frac{1}{2})$ in the molecular magnetic field. The heats of dissociation will then be given, since $\text{Z}_e{}^2 = 22 \cdot 05$, with $\cos\theta = 1$, by

$$\text{Q} = \frac{310 \cdot 2}{3} \cdot 22 \cdot 05\left[\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}\right] \cdot \frac{1}{2[2-\frac{1}{2}] \, . \, 1} \cdot$$

Table II. gives all the data required for the calculation of the heats of dissociation together with the theoretical and observed values. The latter are taken from Landolt and Börnstein's Tables (edn. 4) unless otherwise stated.

TABLE II.

Heats of dissociation of monovalent gaseous elements.

Element.	Z_e^2.	n_1.	n_2.	k.	cos θ.	Q calc.	Q found.
H	1	1	2	1	1	77·55	81, 85
F	22·05	2	3	2	1	316·5	?
Cl	„	3	4	2	1	110·6	113·0
Br	„	4	5	2	1	51·3	55·3
I	„	5	6	2	1	27·9	36·86

The agreement is sufficiently remarkable, considering the errors involved in practical measurements, to warrant the feeling that the theory is on sure ground. All the values appear to be low, divergencies increasing with the molecular weight, as might be expected. Of the possible values of cos θ we have selected the value 1; arbitrariness may be avoided, however, by adopting a provisional hypothesis which is applied consistently in what follows. This is that the components of moment of momentum of all *active* valency orbits in the direction of the field of the second atom, or other half of the molecule, shall be equal to the moment of the bond electron. This is expressed in the formula

$$(k-\tfrac{1}{2}) = \sum_{s}(k-\tfrac{1}{2})\cos\theta, \quad . \quad . \quad . \quad . \quad (10)$$

where s is the number of active valency orbits. In the case of the halogen elements s is 1, so cos θ is also necessarily unity.

The same method, with the hypothesis expressed in (10), will now enable us to calculate the Runge denominator for more complicated molecules where the moment of the trunk may not be zero as in the cases so far discussed. The number of "active" valency electrons in an atom is in general equal to the principal valency of the element. The $p-s$ valency electrons are assumed to lock up together with the trunk into a configuration of zero moment. With nitrogen we shall then have $2k_1=p-s$ and $3k_2=s$; with oxygen, $4k_1=p-s$, $2k_2=s$; with the halogens possibly $4k_1+2k_2=p-s$, $1k_2=s$. Following Sommerfeld in his explanation of the anomalous Zeeman effect of doublet and triplet atoms, we then suppose that the direction of the moment of the bond orbit is defined by an angle θ_1; the remaining $s-1$ "active" valency orbits are considered to be associated with the trunk in such a way that the moment of the whole complex [trunk $+(s-1)$ valency orbits] is given by the sum of the individual moments and is defined in direction by the common angle θ_2. The moments of all active valency orbits will be affected in the same way by change in their azimuthal quantum numbers by $\frac{1}{2}$. A corresponding number of $\frac{1}{2}$ units represents the gain in moment of the trunk. The total moment of the trunk will also depend on the impulses received in the other half of the molecule, which may differ in sign. Thus in the case of the halogen elements the trunk receives an impulse of $+\frac{1}{2}$ in one half of the molecule and $-\frac{1}{2}$ in the other; the total moment is therefore zero, as has been assumed above.

The magnetic energy of the half molecule will now be made up of three parts:—

(1) The energy of the "outer" or bond electron in the field of the other half of the molecule. If θ_1 defines the direction made by the vector normal to this orbit with the direction of H, this energy will be equal to $(k-\frac{1}{2})\mathrm{BH}\cos\theta_1$.

(2) The energy of the inner complex in the field H. If T′B represents the moment of this complex and θ_2 the angle its direction makes with H, this energy will be represented by an amount $\mathrm{T'BH}\cos\theta_2$.

(3) The energy of strain between the inner complex and the bond electron. In magnitude the field of this electron will be equal to that of the second atom. If θ represents the angle between the moment of the inner complex and the field of the bond electron, this energy will be $\mathrm{T'BH}\cos\theta$.

Summing these amounts and substituting for H in terms of $\Delta\nu_{\text{norm.}}$ by (7), we have

$$\mathrm{E}_a' = 2\{(k-\tfrac{1}{2})\cos\theta_1+\mathrm{T}'(\cos\theta_2+\cos\theta)\}\,.\,h\Delta\nu_{\text{norm.}}. \quad (11)$$

The resultant moment of all orbits in the direction of H must, however, be equal to that of the bond electron by (10). Thus if T represents the moment of the trunk, as distinct from that of the complex (trunk inner valency electrons), we have

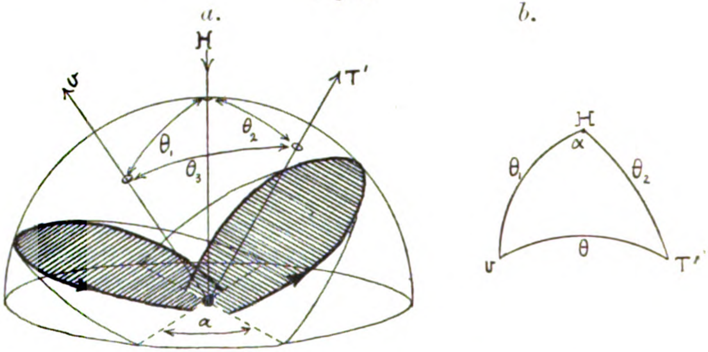
$$(\mathrm{T}'-\mathrm{T})\cos\theta_2+(k-\tfrac{1}{2})\cos\theta_1 = (k-\tfrac{1}{2}). \quad . \quad (12)$$

(10) may now be written

$$\mathrm{E}_a = 2\{(k-\tfrac{1}{2})+\mathrm{T}\cos\theta_2+\mathrm{T}'\cos\theta\}h\Delta\nu_{\text{norm.}}. \quad . \quad (14)$$

A relation between the angles θ θ_1 and θ_2 may now be obtained by demanding that the orbits and trunk shall be in equilibrium so that a small displacement will result in no energy change. In diagram 1, *a* represents the arrangements of orbits on one side of the equatorial plane of a molecule, *b* represents a stereographic projection of the points where the vectors concerned pierce a sphere surrounding the molecule. *v* represents the vector normal to the bond orbit, H the field of the second atom, and T′ the inner complex.

Fig. 1.



The angles of the spherical triangle will then be related as follows:

$$\cos\theta = \cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos\alpha. \quad . \quad (15)$$

Substituting for $\cos\theta$ in (14), we have

$$E_a = 2\{(k-\tfrac{1}{2}) + T\cos\theta_2 + T'(\cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos\alpha)\}h\Delta\nu_{\text{norm.}}. \quad (16)$$

The conditions for equilibrium of orbits and trunk may be written

$$\frac{\partial E_a}{\partial\theta_2} = \frac{\partial E_a}{\partial\alpha} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

This requires that $\cos\alpha = 1$, and gives the following relation between the angles θ_1 and θ_2,

$$\tan\theta_2 = \frac{T'\sin\theta_1}{T + T'\cos\theta_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Expressing all angles in (16) in terms of θ_1, we have

$$\frac{E_a}{2} = (k - \tfrac{1}{2} + \sqrt{T^2 + 2TT'\cos\theta_1 + T'^2})h\Delta\nu_{\text{norm.}} \quad . \quad . \quad . \quad (19)$$

As examples of the use of formula (19) we may consider first the union of the elements oxygen and nitrogen. Effectively we regard the two atoms of the molecule as linked by a single "bond" and calculate the Runge denominator by considering the moment of the inner electron and trunk. In the case of oxygen there are two active valency electrons, i. e. $s=2$. The moment of the trunk will then be $\frac{1}{2}+\frac{1}{2}=1=T$. Since there is one "inner" valency orbit, $T'=1+3/2$. If we substitute the value of θ_2 of (18) in equation (10) we obtain a complicated cubic. Considering the order of accuracy attainable in the empirical results by which we shall test our theoretical deductions, it will be sufficient for the present to determine the limits between which the Runge denominator must lie. If we call the expression under the square root in (19) X, we obtain the following values for corresponding values of $\cos\theta_1$ shown:

$\cos\theta_1$.	X.
1	7/2
2/3	3·258
1/3	2·986
0	5/2

We may legitimately reject the value for $\cos\theta=0$. The heat of dissociation will then be given by

$$Q=\frac{17{\cdot}4}{3}\left(\frac{1}{4}-\frac{1}{9}\right)\cdot\frac{1}{r},$$

where

$$r=2(\tfrac{3}{2}+X).$$

Substituting the values of X calculated above, we obtain the values $Q=24{\cdot}99$, $26{\cdot}27$, or $27{\cdot}85$. The experimental value is 26·0, which is mid-way between our theoretical limits.

Using a precisely similar method for nitrogen where $T=3/2$, $T'=3/2+2(3/2)$, we obtain for r:

$\cos\theta_1=1$	$r=15$	$Q=12{\cdot}57$
2/3	14·23	13·25
1/3,	13·39,	14·08.

The value found is 13·0; again our theoretical values approximate closely.

So far we have confined ourselves to symmetrical compounds. In the case of the halogen hydracids we assume that the moment of the trunk becomes $\frac{1}{2}$ due to the change of the k_2 halogen orbit, and $-(-\frac{1}{2})$ for the hydrogen. T thus becomes unity and $T=T'$, since there are no other orbits free in the molecule but the bond orbit. X is 2, and r is therefore given unambiguously as $2(3/2+2)=7$.

Table III. gives all the data for the calculation of the theoretical heats of dissociation according to the formula

$$Q=\frac{A}{3}\cdot\frac{1}{7}\left(\frac{22\cdot05}{n_2^2}-\frac{1}{1}\right),$$

together with the experimental values.

TABLE III.

Heats of dissociation of halogen hydracids.

Acid.	n.	n.	k.	$\cos\theta_1$.	r.	Q calc.	Q found.
HF	1	2	2	1	7×2	33·3	38·5
HCl	1	3	2	1	7	21·4	22·0
HBr	1	4	2	1	7	5·43	8·6
HI	1	5	2	1	7	−3·5	−6·4

Except in the case of hydrofluoric acid, where it is necessary to increase the Runge denominator to twice its value, the theoretical results agree satisfactorily in magnitude and sign with experimental results. The abnormality of HF is not surprising; we may suppose the heat change represents the formation of two molecules. This tallies with the chemical evidence. It is particularly satisfactory that the sign of the reaction reverses precisely at the point where the natural frequency of the halogen becomes smaller than that of hydrogen. It is not advisable at present to advance a general rule for the determination of the sign of the heat change until more reliable data are forthcoming. It may be noted, however, that the necessity for the atom of highest valency (the "key" atom) to *diminish* in frequency under the influence of the molecular field, implies negative values in the case of H_2Te, SbH_3, and Cl_2O, as are observed; but AsH_3 and H_2Se appear to be exceptional, if the empirical figures can be relied on, which is certainly very doubtful in the case of AsH_3. The consistently negative values for unsaturated compounds are explicable in another manner and will be dealt with in a future communication.

In the case of water the moment of one OH trunk will be zero, since it receives the impulse $+\frac{1}{2}$ from the O orbit and $-\frac{1}{2}$ from the hydrogen. Since we are dealing with a bivalent key atom we must take into account the second orbit.

We may reasonably assume that this will be equal to the sum of the moments of the oxygen and hydrogen orbits, *i.e.* $3/2-\frac{1}{2}=1$. We thus get $r=2(3/2+1)=5$. The formula

$$Q=\frac{A}{3}\cdot\frac{1}{r}\left(\frac{17\cdot4}{4}-\frac{1}{1}\right),$$

then gives $Q=69\cdot2$ Cal. The value found is 69·0.

Applying the same method to ammonia, we must recognize that the symmetry factor will no longer be two, but three, as there are three separate bonds to be considered. The nitrogen will receive $+3(\frac{1}{2})$ from its $3k_2$ valency orbits, the hydrogen (only one must be considered as we are calculating the energy of one bond) will contribute $-(-\frac{1}{2})$, so T will be 2. There are two loose valency orbits each of moment $3/2-\frac{1}{2}$, so T′ becomes 4. r will now be $3(3/2\times X)$. The following are the values of r and Q for the assumed values of $\cos\theta_1$:—

$\cos\theta_1 =$	$r =$	$Q =$
1	22·5	10·48
2/3	21·11	11·17
1/3,	19·59,	12·04.

The experimental value is 11·89.

In Table IV. are given E_a, and the observed heats of formation $Q_{obs.}$, for the trivalent compounds shown. In the fourth column values of r are given which would reduce the theoretical value E_a to the Q's shown in the fifth column.

TABLE IV.

Compound.	E_a.	Q obs.	r.	E_a/r.
NH_3	235·8	11·89	20	11·79
PH_3	47·57	4·9	10	4·8
AsH_3	−18·55	44·2 ?	?	?
SbH_3	−49·1	−33·96	3/2	−33·4
BF_3	418·3	234·6	3/2	278
BCl_3	101·63	89·1 ?	?	
PCl_3	102·5	69·7	3/2	68·32

It will be noted that the value of r which it is necessary to assume in the case of PH_3 is very approximately $\frac{1}{2}$ of the theoretical value for ammonia. With other compounds on which any reliance can be placed, the value of r seems to sink to 3/2. This is the value r would assume theoretically if the impulses were distributed in such a way that the moment of the trunk were zero, and a numerator were introduced which would cancel the symmetry factor of 3. This will be referred to again when considering the phenomena of quadrivalent compounds.

With carbon we assume there are two electrons in k_1, and two in k_2 orbits. If all are active this implies that the impulse received by the trunk from two of them will neutralize that received from the other two. The Runge denominator should then be simply $4(3/2)=6$. Here we assume T′ is also zero, since the most symmetrical arrangement of the valency orbits which also satisfies the requirements of equation (10) is that in which there are three bonds in the $\cos\theta=1/3$ position on one side of the equatorial plane, and one at $\cos\theta=1$ on the other. Both halves of the molecule then obey the condition that the components of momentum in the direction of the field (at right angles to the equatorial plane) shall be equal to $k-\frac{1}{2}$. Table V. gives observed and calculated values of various quadrivalent compounds.

TABLE V.

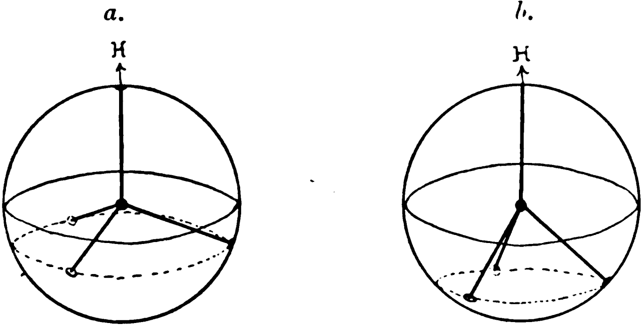
Compound.	E_a.	Q obs.	r.	q.	Q calc.
CH_4	135·6	20·35	6	1	22·6
CCl_4	42·81	21·03	6	3	21·4
SiF_4	464·0	239·8	6	3	232·0
$SiCl_4$	146·8	121·8	?	?	?

The theoretical value for CH_4 agrees well: with the others the numerator, designated q, which it is necessary to assume appears to be 3. Although the numerator is purely arbitrary, the fact that for similar types of compounds it tends to reduce to the same number would indicate that the agreements then obtained are not entirely accidental. The factor q appears to be connected with the ratios of the principal quantum numbers of the linked orbits, but more cannot be said on this point till further evidence is available.

Structural considerations.—The fact that the disposition of orbits in the carbon atom will depend only on their mutual interactions, without interference by the moment assumed by the trunk, is apparently responsible for the characteristic chemical properties of this element. Stereoisomerism is evidently dependent on the quantized angles adopted by the bond orbits. The transmission through a long chain of a property imposed by a substituent would also seem to be possible only when the moment of the trunk does not interfere. With oxygen and nitrogen where energy is locked up between trunk and orbits, the configuration will not have the freedom possible in the case of saturated carbon. Since the hypothesis expressed in equation (10) restricts the possible angles which can be assumed by the orbits to the values $\cos\theta_1=1$, $2/3$, and $1/3$, when the trunks have no moment they must lie in the plane of the common orbits. Thus the spatial quantizing of the orbits necessarily implies in the case of carbon the definite orientation of the trunks.

As has been stated, the most symmetrical arrangement of orbits in carbon is that illustrated in fig. 2 (*a*), where three bonds at $\cos\theta_1=1/3$ are in equilibrium with one at $\cos\theta_1=-1$. Each of the angles between bonds then becomes the well-known "tetrahedral" angle 109° 28′.

Fig. 2.



If, on the other hand, the moment on one side of the equatorial plane is altered so that it becomes equal to $3/2+1/2=2$, the remaining three bonds on the other side must adopt the $\cos\theta_1=2/3$ position as shown in fig. 2 (*b*). The angle θ_1 now becomes 131° 47′. It is therefore a definite consequence of the theory that the "tetrahedral" angle is not the only angle which must be taken into account in explaining the stereoisomerism of carbon compounds. If we consider a chain of carbon atoms united by bonds forming these two angles with the direction of the field, which will be at right angles to the length of the chain (fig. 3, *a* and *b*), the distance between each successive carbon atom will be proportional to $\sin(\cos^{-1} 1/3)$ and $\sin(\cos^{-1} 2/3)$ respectively. The ratio of these numbers will represent the relative rate of increase in length of a carbon chain connected by bonds at these angles.

From X-ray measurements, quoted by Bragg (Trans. Farad. Soc. Discussion, 1923, p. 478), Muller and Shearer have shown that the molecules of fatty esters orientate themselves in thin films in such a way that their length is at right angles to the surface, "like the stalks of growing corn." Increase in the length of the acid end of the molecule produces an increase in thickness at a different rate from increase in the alcohol radicle. They find that these increases are in the ratio

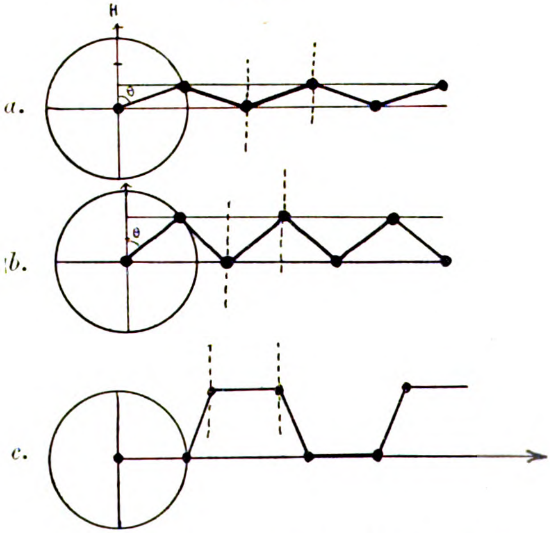
$$\frac{2 \text{ acid radicle carbons}}{1 \text{ alcohol ,, carbon}} = \frac{1\cdot 94}{1\cdot 22} = 1\cdot 59.$$

If we identify the bond angle characteristic of the acid end of the molecule with the $\cos\theta = 2/3$ position, we should have theoretically,

$$\frac{2 \text{ bonds at } \cos^{-1} 2/3}{1 \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad 1/3} = \frac{2 \times \sin(\cos^{-1} 2/3)}{\sin(\cos^{-1} 1/3)},$$

$$\frac{2 \times 0\cdot 7455}{0\cdot 9428} = 1\cdot 58.$$

Fig. 3.



This is a remarkable agreement which affords definite experimental support to the consequence of this theory which demands three possible bond angles for carbon. The explanation suggested by Bragg (*loc. cit.*) is inherently improbable as it denies the possibility of free rotation about a single bond. This will be clear from a comparison of *a*, *b*, and *c* in fig. 3. The bonds in *a* and *b* are free to rotate about the dotted lines without distortion of the bond angle, or alteration in the distance between carbon atoms. Free rotation in *c* must produce the same length of chain as in *a*.

The insight into structural relations of carbon compounds which the theory affords will be developed in a paper to follow shortly. The treatment of the polar link, which, as has been stated, stands in the same relation to the non-polar link treated above as does the Stark effect to the Zeeman effect, has been worked out satisfactorily, and will follow as Part II. of this series.

Note.—Since the original of this paper, and those to follow, was written, the author has considered the application of the extremely interesting theory of the quantum relation published by de Broglie (Phil. Mag. xlvii. p. 446, 1924). It is worth noting here that the fundamental principle of the synchronization of bond orbits follows directly from de Broglie's generalization that for stable orbital motion "the phase wave is tuned with the length of the path."

Simla,
August 1924.

XXXVIII. *Short Electric Waves obtained by the use of Secondary Emission.* By E. W. B. Gill, *M.A.*, *B.Sc.*, *Fellow of Merton College, Oxford,* and J. H. Morrell, *M.A.*, *Magdalen College, Oxford* [*].

IN a previous communication (Phil. Mag. July 1922) the authors gave an account of some experiments on the production of continuous oscillations of short wavelengths of the order of a metre by gas-free valves, and put forward a theory to account for their maintenance. The theory was only worked out for the case where the electron currents through the valves were small and the space charges between the electrodes negligible, if the currents are large the theory would have to be modified.

In all cases, however, the main conclusion was correct, that if the time T that the electrons in the valve take to pass from one electrode to another is comparable to the time *t* of oscillation of the attached circuits, then a control electrode as usually employed is not necessary, since for certain values of the ratio T/*t* the motion of the electrons will vary in such a way that they maintain the oscillations.

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[*] Communicated by Prof. Townsend.

These considerations lead to the fact that a particular applied voltage maintains most strongly an oscillation of a particular wave-length: a species of "tuning" which is non-existent for longer wave-lengths maintained by the more usual methods.

In the first experiments the oscillations were produced in a Lecher wire system attached to the grid and plate of a 3-electrode valve, the filament and plate being at about the same potential and the grid several hundred volts positive to them; this method of short wave production was discovered by Barkhausen and Kurz (*Physikalischer Zeitschrift*, Jan. 1920). In this arrangement the electrons moving from the filament are accelerated in the space between the filament and the grid, and are retarded between the grid and the plate.

In the experiments to be described the grid has still the highest positive potential, but the plate, instead of being at about the same potential as the filament, is also at a fairly high positive potential. In this case all the electrons which pass through the grid reach the plate whether oscillations are occurring or not, and the secondary emission from the plate becomes of importance.

It may be convenient to state briefly the main effects of secondary emission in a 3-electrode valve.

If in such a valve the grid is maintained at a fixed high positive potential V_g above the filament [*], and the plate current is found for various plate potentials V_p above the filament, the relations between the plate current and the plate potential are given by curves as in fig. 1, as found originally by Hull [†]. In these curves the negative current through the valve to the plate is plotted upwards.

The electrons move from the hot filament to the grid under an accelerating potential V_g, those which pass through move on to the plate under a retarding potential $V_g - V_p$ and strike the plate with the velocity acquired by falling through a potential difference V_p. As a result of this impact secondary electrons are emitted from the plate with a negligible velocity and move to the grid under the accelerating potential $V_g - V_p$. The reduction of the current with increase of plate potential, as shown by the curves, is due to this emission. As the velocity of impact (which depends only on V_p) is increased the number of secondary electrons increases.

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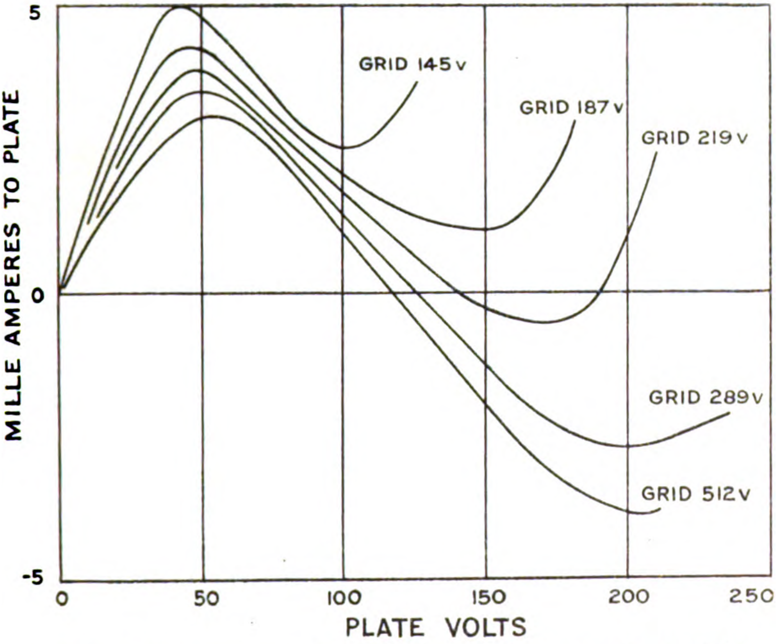
[*] In this paper the filament is taken as at zero potential, the voltage drop down it is neglected, and no account is taken of velocities of emission or contact differences of potential.

[†] Hull, Proc. Inst. Radio Engineers, Feb. 1918.

It is not necessary to discuss the upward bend of the current when V_p is further increased, as the oscillations to be described could not be maintained for values of V_p in this region *.

Fig. 1.



The downward portions of the curves are nearly straight lines and it is very fairly accurate to assume, as will be done, that the number of secondary electrons set free by n primary electrons, if the plate potential is V, is proportional to nV.

It should be noted that for the filament emissions and particular values of V_g and V_p used, none of the electrons emitted from the filament return to it and none of the secondaries return to the plate. The voltages are sufficient

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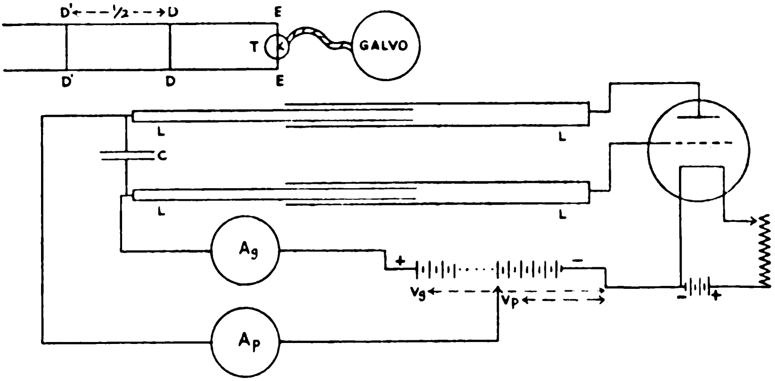
* A detailed explanation of the curves is given in Phil. Mag. May 1923, p. 864.

to collect the saturation currents, both from the filament and the plate, and the space charges, although they modify the fields due to the fixed potentials V_g and V_p, cannot be the ultimate cause of the maintenance of oscillation. The case is therefore entirely different from the usual methods of producing oscillations by valves in which the control of the space charge by the grid potential is the essential feature.

Two types of 3-electrode valves were used in the experiments:—A Marconi MT 5 type (described in detail, Phil. Mag. July 1922, p. 165), and a Marconi LS type which has a tungsten filament, the grid is a spiral of molybdenum wire of diameter 5 mm., and the plate is a cylinder of nickel of diameter 10 mm. The LS is smaller than the MT 5, which has a grid 10 mm. in diameter and plate 25 mm. diameter.

The circuits used are shown in fig. 2.

Fig. 2.



The oscillatory system consisted of two Lecher wires L L attached respectively to the grid and the plate of the valve, the other ends of the wires being bridged by the condenser C of about 1 mmf. capacity. The length of the Lecher wires was adjustable, each being made of a telescopic tube sliding over a rod.

The oscillatory system thus comprised distributed inductance and capacity of the wires and concentrated capacities at both ends; the plate and grid of the valve forming a small cylindrical condenser.

The condenser C was by far the largest capacity in the circuit, so that its terminals may be regarded as potential nodes for any oscillation in the system and suitable points for attaching the leads to the high potential battery. This high potential battery was used to maintain the grid at a high positive potential V_g above the filament (negative end) and the plate at a positive potential V_g less than V_p, milliammeters $A_g A_p$ indicated the currents flowing to the grid and plate respectively.

The wave-lengths and relative magnitudes of any oscillatory currents set up were determined by means of a secondary circuit loosely coupled to the valve circuit. This secondary circuit also consisted of Lecher wires L, L, about 10 cm. apart, bridged at one end EE by wires to the heater coil of a Paul thermo-couple T, which had a sensitive galvanometer attached to the thermo-couple. The wires were also bridged by a sliding bar DD.

The method of carrying out an experiment is the following. The filament is heated to a suitable brightness, and a simple preliminary test made to see if oscillations are occurring in the Lecher wire system attached to the valve; this is easily done by touching various points of the wires with the hand. If oscillations are taking place this process damps them and the readings of the milliammeters AA change.

If this test indicates that there are no oscillations, the telescopic rods are pushed in or out till a sudden change in the readings of the milliammeters indicates that oscillations have commenced. The bar DD is now moved along the secondary circuit, and when the circuit DEED is in tune with the primary the galvanometer attached to T shows its maximum deflexion; it will reach a second maximum when DD is moved a further distance $\lambda/2$, λ being the wave-length.

The use of the secondary circuit gives the wave-length of the primary oscillation, and the maximum galvanometer deflexion is proportional to the square of the primary current provided the relative positions of the two circuits are always the same.

It would have been simpler to measure the magnitude of the primary oscillatory current direct by inserting the thermo-junction in that circuit, but it was found that the resistance of the junction made the maintenance of the oscillation, which was always very feeble, extremely difficult.

By experiments of the type outlined above it was found that for a fixed value of V_p and V_g oscillations could be maintained over a certain range of wave-lengths (just as the authors found for the Barkhausen short waves).

Thus with the MT 5 valve the grid charged to 312 volts positive to the filament and the plate to 127 volts; it was found that oscillations could be sustained from $\lambda=176$ cm. to $\lambda=194$ cm. For 176 cm. the oscillation was just detectable: as λ was increased the amplitude of the oscillation increased till at 188 cm. it reached its maximum. From 188 cm. to 194 cm. the amplitude decreased.

For a larger electron emission from the filament the range of wave-lengths over which oscillations could be sustained was increased, but the maximum oscillation still occurred at about $\lambda=188$.

Confining attention now to the wave-length of the oscillation with the maximum current amplitude, the next point to be investigated was how λ depends on the potentials of the electrodes.

The result of many experiments with the LS valve done in the method described indicated :—

(A) That if V_g-V_p was kept constant the wave-lengths of strongest oscillation were within errors of experiment independent of the absolute values of V_g and V_p.

Thus with the LS valve the values of λ found under such a condition were :—

V_g.	V_p.	V_g-V_p.	λ in cm.
122 volts	38	84	101·6
164	78	86	99·4
208	122	86	98·6

(B) That if V_p was kept constant and V_g-V_p varied, then $\lambda^2(V_g-V_p)$ was constant within errors of experiment.

Thus with LS valve for V_p constant and various values of V_g-V_p, the values of λ and of $\lambda^2(V_g-V_p)$ were :—

V_p.	V_g.	V_g-V_p.	λ.	$\lambda^2(V_g-V_p)$.
160	244	84	94·6 cm.	751×10^3
160	272	112	82·1	754 „
160	291	131	73·6	748 „
160	299	139	74	761 „

(C) As mentioned previously, oscillations could not be maintained if V_p was so nearly equal to V_g that the corresponding point in fig. 1 was to the right of the downward portion of the curve.

The combination of A and B indicates that whatever the values of V_g and V_p the wave-length λ depends only on V^g-V_p in accordance with the formula $\lambda^2(V_g-V_p)=\text{const.}$

This suggests that the electrons responsible for the maintenance of the oscillations are the secondary electrons which go from the plate to the grid as their time of passage depends on $V_g - V_p$ only. For the primary electrons pass from the filament to the grid in a time which depends on V_g, they pass through the grid with a velocity depending on V_g, and their time from the grid to the plate depends therefore on V_g as well as on $V_g - V_p$.

The following calculations show that oscillations of the type observed can be maintained by the secondary electrons.

The energy conditions for the maintenance of an oscillation are simple. If an oscillation is started in the circuits connected to the valve, alternating potential differences are set up between the electrodes. The electrons moving across the valve are acted on by these alternating potentials as well as by the fixed potentials applied to the electrodes. If the alternating potentials do work on the electrons, this work is done at the expense of the energy of the oscillations and in consequence the oscillations are damped out; if, on the other hand, the work done by the alternating potentials on the electrons is negative, the oscillation will be sustained. The electrons in this latter case give energy to the oscillating circuit which can be sufficient to compensate it for resistance and radiation losses.

(When the oscillations are being sustained the electrons hit the electrodes with less velocity than when there are no oscillations; the heating of the plate is thus less in the former than the latter case, and the difference represents the work available for the maintenance of the oscillations.)

It may be assumed that the alternating potential between plate and grid is $V_0 \sin pt$, with periodic time $\dfrac{2\pi}{p}$.

The filament is joined to potential nodes on the Lecher wire system, and its potential being taken at zero, the total plate potential at time t is $V_p + \frac{1}{2}V_0 \sin pt$, and the total grid potential is $V_g - \frac{1}{2}V_0 \sin pt$.

The following simplifying assumptions will be made:—

1. V_0 is so very small compared with V_p and V_g that the time the electrons take to move between the electrodes is determined only by V_p and V_g, not by V_0.
2. The plate and grid will be regarded not as concentric cylinders but as parallel planes at distance d apart.
3. The secondary electrons will be supposed to leave the plate with zero velocity and to move direct from the plate to the grid and none to pass through the grid.
4. The effect of space charges will be neglected.

The electrons moving across the valve can be divided into three classes. The first, those which go direct from the hot filament to the grid; the second, those which go from the filament to the plate; the third, the secondary electrons which return from the plate to the grid.

It can be shown that the work done per cycle by the alternating potentials is zero for both the first and the second class, and it is only necessary therefore to consider the last class.

Let T be the time the secondary electrons take to pass from the plate to the grid, which in accordance with assumption 1 is the same for all and is equal to

$$d\sqrt{\frac{2m}{e(V_g-V_p)}}.$$

The electron which leaves the plate at time t_0 has at time t a velocity given by

$$\frac{dx}{dt}=f(t-t_0),$$

where

$$f=\frac{e}{m}\frac{V_g-V_p}{d},$$

the axis of x being normal to the plate.

The work done by the alternating potential $V_0 \sin pt$ as the electron moves from the plate to the grid is

$$-\frac{eV_0}{d}\int_{t_0}^{t_0+T}\sin pt \, . \, dx,$$

which on integration becomes

$$-\frac{feV_0}{d}\left\{\frac{\sin p(t_0+T)}{p^2}-\sin pt_0-\frac{T\cos p(t_0+T)}{p}\right\}. \quad (1)$$

If the electrons left the plate in a uniform stream the average value of the expression (1), t_0 being regarded as the variable and having values from 0 to $2\pi/p$, would be zero.

The secondary stream is not however uniform, for as t varies the primary electrons hit the plate at different velocities corresponding to falling through a potential drop of $V_p+\frac{1}{2}V_0\sin pt$. Remembering that the number of secondary electrons emitted for each incident primary is approximately proportional to the potential through which the incident electron has fallen, the number of secondaries given off between time t_0 and t_0+dt_0 is proportional to

$$(V_p+\tfrac{1}{2}V_0\sin pt_0)\,dt_0. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The work done per cycle by the alternating potential on the secondary electrons is therefore proportional to the integral between $t_0=0$ and $t_0=2\pi/p$ of the product of expressions 1 and 2. Omitting certain constants, the work per cycle is thus found to be proportional to

$$-\frac{1}{p^3}\{\cos p\mathrm{T}-p\mathrm{T}\sin p\mathrm{T}-1\},$$

or the work *per second* is proportional to

$$-\frac{1}{p^2}\{\cos p\mathrm{T}+p\mathrm{T}\sin p\mathrm{T}-1\}.$$

Hence, if T_0 is the time of one oscillation, $\mathrm{T}_0=2\pi/p$ and the work is proportional to

$$-\mathrm{T}_0^2\left\{\cos 2\pi\frac{\mathrm{T}}{\mathrm{T}_0}+2\pi\frac{\mathrm{T}}{\mathrm{T}_0}\sin 2\pi\frac{\mathrm{T}}{\mathrm{T}_0}-1\right\}.$$

The energy communicated to the oscillating system per second by the electrons is therefore proportional to

$$\mathrm{T}_0^2\left\{\cos 2\pi\frac{\mathrm{T}}{\mathrm{T}_0}+2\pi\frac{\mathrm{T}}{\mathrm{T}_0}\sin 2\pi\frac{\mathrm{T}}{\mathrm{T}_0}-1\right\},$$

and oscillations will be maintained if this expression is positive and the energy is equal to that lost by resistance and radiation.

If V_g and V_p are kept constant, T, which is proportional to $\frac{1}{\sqrt{\mathrm{V}_g-\mathrm{V}_p}}$, is constant, and the wave-lengths which can be maintained are those for which T_0 makes the above expression positive.

Keeping T constant, the variations of the value of this work function as T_0 is varied are given in the following table:—

Value of $\frac{\mathrm{T}_0}{\mathrm{T}}$.	Value of function.	Value of $\frac{\mathrm{T}_0}{\mathrm{T}}$ for maximum energy.	Value of $\frac{\mathrm{T}_0}{\mathrm{T}}$ for zero energy.
∞ to 2·7	Positive and decreasing.	$\frac{\mathrm{T}_0}{\mathrm{T}}=\infty$	$\frac{\mathrm{T}_0}{\mathrm{T}}=2{\cdot}7$
2·7 to 1	Negative.	……	$\frac{\mathrm{T}_0}{\mathrm{T}}=1{\cdot}0$
1·0 to ·66	Positive.	$\frac{\mathrm{T}_0}{\mathrm{T}}=0{\cdot}8$	$\frac{\mathrm{T}_0}{\mathrm{T}}=0{\cdot}66$

and so on alternately positive and negative.

If for convenience we call λ the wave-length of the oscillation whose periodic time is T, then the energy conditions are suitable for the maintenance of all waves longer than $2{\cdot}7\lambda$; not suitable for waves between $2{\cdot}7\lambda$ and λ, suitable for waves from λ to $\cdot 66\lambda$ and so on, while with regard to the range from λ to $\cdot 66\lambda$ the wave-length which is most strongly regenerated is $\cdot 8\lambda$.

It is this range which the preceding experiments have evidently covered; for we found that a small range of wave-lengths was maintained. Further, as the strongest regeneration occurs for the particular value $\cdot 8$ of $\frac{T_0}{T}$, we should expect that if T is altered the wave-length of maximum amplitude should alter in the same ratio, but T is proportional to $\frac{1}{\sqrt{V_g - V_p}}$, and it is therefore to be expected that the wave-length of maximum amplitude should also be proportional to $\frac{1}{\sqrt{V_g - V_p}}$, which was found to be true.

The broadening of the range if the filament is heated more brightly is accounted for by the fact that more electrons leave the filament per second and more energy is therefore available to compensate for the oscillation losses. The theory indicates that there should be other ranges of still shorter wave-length maintained which we did not get experimentally; but this was to be expected, as the energy losses increase enormously as the wave-length gets very small.

With regard to the longer wave-lengths it was from the outset probable that these would be maintained as the circuit is a modified form of Hull's well-known "negative resistance" method of producing continuous oscillations.

A final test was made with the MT 5 valve with $V_g - V_p =$ 180 volts, and it was found that wave-lengths above 33 metres, and below this the range from 1·94 metres to 1·76 metres, could be maintained.

The general experimental results that all wave-lengths above a certain value, and a range of shorter wave-lengths, can be maintained are in good agreement with the theory. The agreement when numerical values are calculated is not so good. In the first place, the gap between the shortest long wave maintained and the best maintained short wave is larger than would be expected from the theory, and in the second place, if the time T that an electron takes to pass from the plate to the grid is calculated from the valve dimensions the ratio $\frac{T_0}{T}$ for the best maintained short wave is not ·8 as the theory gives, but about 2 for the LS valve and 3 for the MT 5.

With regard to the first point, the simple theory gave an expression for the work put into the oscillatory circuit per second for different wave-lengths for a specified amplitude V_0 of alternating potential between the grid and the plate. This work must be equal to the resistance and radiation losses per second for the oscillatory current corresponding to this value V_0. For a small variation in wave-length this current is proportional to V_0, but this is not the case for large variations of the wave-length, as the distributed capacity of the wires must be taken into account. It does not necessarily follow therefore that if the work function has a particular value for a short wave-length which is maintained, that the long wave for which the work function has the same value will also be maintained.

With regard to the second point, it is probable that the assumption that none of the secondary electrons pass through the grid chiefly accounts for the discrepancy, and that many of them pass backwards and forwards once or twice through the grid before being collected on it,—in fact the theory on which the calculations are based can only be expected to account for the main features of the experiments.

We are very much indebted to Professor Townsend for help and advice in these experiments.

XXXIX. *On the Discriminations between Past and Future.*

By P. Du Val *.

THIS paper is intended to supplement and develop some remarks on the subject in my "Geometrical Notes on de Sitter's World" (Phil. Mag. May 1924).

In the first case it is important to notice that the consciousness of an observer is related to his past and his future in ways far more strikingly different than the mere geometry of the question would lead us to suppose.

Thus, his world-line passes at the "present instant" through the vertex of the light-cone, being within the cone

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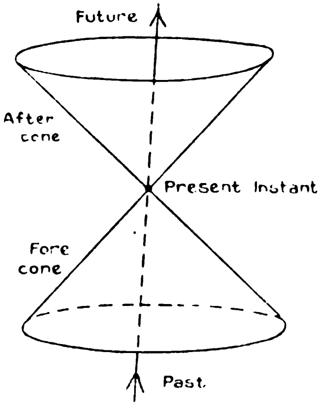
* Communicated by the Author.

on both sides of the vertex, as in fig. 1. Both cone and world-line are divided at the vertex into two portions extending to infinity, one segment of the line being within each sheet of the cone and outside the other.

Now, of course, most observers can by the exercise of their intellectual faculties form some conception of what events lie in various parts of the world, both on and off their own world-lines; but each observer has a peculiarly distinct consciousness, quite intuitive and arrived at without logical procedure, of certain events which can only be regarded as forming a part of the "here and now" of his perceptual experience.

Fig. 1.



These are the events of one sheet of his instantaneous light-cone, which we call the fore-cone, and of one segment of his world-line, which we call the past segment, the past segment of the world-line being that one which lies inside the fore-sheet of the cone (fig. 1). The observer's perceptions of these two loci of events, superficially very dissimilar—one being what we call memory and the other vision—have yet this resemblance, that both are of geometrical loci, abruptly broken off at the "present instant," where the consciousness in each case rises to a maximum of intensity, while it shades off into dimness and ultimate oblivion in the direction of infinity.

This odd fact, that we are conscious of half the events in our light-cones and half those in our world-lines (that is, speaking roughly; of course no one can remember all the past, or see an infinite distance; but we are accustomed to consider hypothetical observers of infinite longevity), which is by no means to be expected from the current geometrical view of the world, is of the utmost empirical importance, having in fact conditioned our whole attitude towards that dependence of events on one another which we call causation. Indeed, it is just our certain intuitive knowledge of events on the past side of us, and our total ignorance (except by inference) of those on the future side, which make us regard the former as fixed, and as determining our present experience, while we regard the latter as depending on the at least partly arbitrary course of our present conduct. To put it more clearly, when we consider the relation between past and present events, we habitually regard the past as argument and the present as function, while in the contrary case we regard the present as argument and the future as function, oblivious of the fact that the relation between function and argument is ordinarily a reversible one, either equally determining the other.

We can bring the fictitious nature of our view of causation home to ourselves by considering a slightly different arrangement. Suppose, for instance, the fore-sheet of the cone to be that which contains the future segment of the world-line; in such a case our present attitude, if adhered to, would force us to conclude that some influence, issuing from our eyes with the speed of light, is a determining cause of the events which we see, since by any ordinary standard of time-measurement we should see them before they happened.

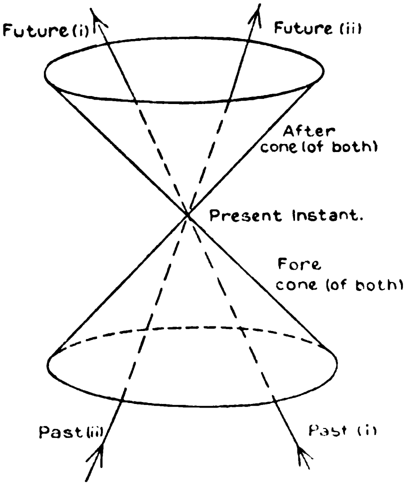
It is thus important, for the understanding of the history of any observer, not only to draw his world-line, and mark on it a scale of proper-time, but to indicate the sense in which this proper-time is to be reckoned. It is also a matter of the first importance whether this sense is determined at random for each observer separately, or whether it depends in some way on the constitution of the world as a whole, and also whether there is any way in which we can define same and opposite senses in two different world-lines. The answers to these questions are of course different in different worlds, but a few general remarks are possible.

For instance, if two world-lines intersect, sameness or opposition of sense in them is perfectly definable with reference to this particular intersection, since they have here the same light-cone, and hence determinately the same or opposite discriminations between its two sheets.

Thus in fig. 2 the observers (i) and (ii) are oriented in the same sense, whereas if the past and future of one of them were interchanged, the fore-cone of each would be the after-cone of the other, and their senses would thus be opposed.

In this connexion, it should be borne in mind that it is quite easy to devise a world in which two world-lines may intersect twice, and that in such a way that senses in them which are the same with reference to one intersection are opposed with reference to the other.

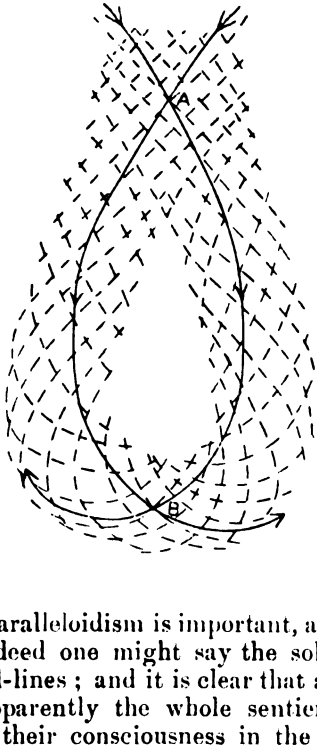
Fig. 2.



For instance, in the world of loop-like connectivity shown in fig. 3 (where the broken lines indicate the general direction of the light-tracks) we can draw two world-lines intersecting at A and B, and give them senses which are the same relatively to the light-cone at A, but opposite relatively to that at B.

Another case in which sameness or opposition of sense is definable is that of two lines which throughout a considerable length have every point of each at a comparatively small distance from some part of the other. Lines thus related we may call paralleloid. Thus, if A in one line is quite close to A′ in the other, and B (distant from A) close to B′ (distant from B), and so for every intervening point, the sense AB may clearly be looked on as the same as A′B′ and opposite to B′A′. In this case again, the sameness or opposition of sense can only be regarded as referring to the region in which the world-lines are paralleloid ; for in a world such as that illustrated in fig. 3, we could draw two lines paralleloid in two regions, and such that senses in them which were the same with reference to one region were opposed with reference to the other. Indeed, a consideration of the figure shows that we could make a world-line to intersect (or to be paralleloid to) itself, such that in whichever sense it is measured, the two intersecting (or paralleloid) parts are oppositely directed.

Fig. 3.

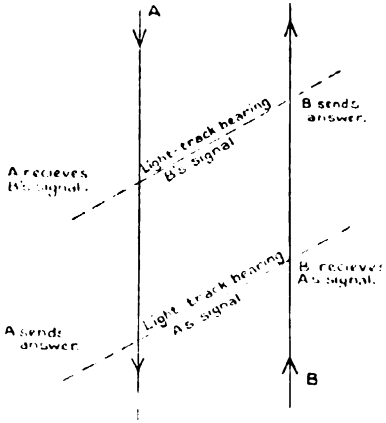


This case of paralleloidism is important, as all the particles of the Earth, indeed one might say the solar system, are in paralleloid world-lines; and it is clear that at least the entire human race, apparently the whole sentient population of the globe, have their consciousness in the same sense. In deciding the merits of any particular world which may be proposed as representing that in which we live, this fact must be borne in mind, and a hypothetical world which offers no explanation of it must be felt to have a very serious disadvantage.

It is an amusing exercise to imagine the case of two observers with oppositely directed consciousness in paralleloid world-lines. No kind of communication is possible between them, since if one sends a signal and the other receives it, it at once (from the point of view of the former) passes into the latter's not-yet-happened-future, and he, ignorant of its nature, even of its existence, cannot possibly answer it.

Fig. 4 may serve to illustrate this. Each of the two observers A, B, receives (the emission of it being on his fore-cone) a visual signal from the other, and at a later instant (from his own point of view) sends off his answer to it. This is a striking instance of the breakdown of our notions of causation, since here each observer regards his own signal as the answer to, *i. e.* as caused by, the other; while neither is conscious of having taken the initiative in the attempt at communication. On a superficial view it would thus appear that the whole thing happened of its own accord, without any external cause, even in the volition of the participants; though of course it will in fact be co-dependent with other events, both before and after it.

Fig. 4.



It is worth considering also the appearance of the world to a human observer whose sense is reversed throughout a finite length of his world-line. (Our knowledge of the laws which govern time-consciousness is hardly sufficient to enable us to rule this possibility out categorically, though I admit it is rather entertaining than probable.) The instant of the first reversal of sense would appear to him to be followed without break by that immediately before the restoration of the original sense, events then proceeding like a cinematograph show in which the film is sent through the lantern wrong end first till the instant of the first change is reached, that being at once followed by the return to normal conditions, and the succeeding events in their proper order. During his period of abnormality a person writing (for instance) would seem to him to pass his pen backwards over the written paper, sucking up every scrap of ink into the nib, so that all trace of what originally appeared written would be removed; if he himself was stunned by a fall, he would (in his own opinion) wake suddenly to the sensation of being flung up from the ground and landed neatly in the spot from which in point of fact he fell; an object knocked down and smashed would be seen first as fragments strewn on the ground, which would with one accord seem to leap together to form the broken object, and rise into its proper position. Such instances could be continued indefinitely.

As for the question how far the sense of an observer's time-consciousness may depend on the general structure of the world, it may be simplified by observing that a world-line in which s is the proper-time will contain in general two "points at infinity," $s=\pm\infty$. All the points at infinity in all the possible world-lines in the world will ordinarily form a three-dimensional locus, though of course in special cases it may degenerate into a surface, a curve, or a point or points. If this locus is such as to supply a determinate distinction between $s=+\infty$ and $s=-\infty$ in every line, each observer's sense is determined by the general structure of the world; not otherwise. There is one other possible case —the world-lines may be re-entrant, without any points at infinity. In such a case it will ordinarily be found possible to construct a three-dimensional locus, cutting each line once, and so providing each with a beginning and end.

Excellent examples of the two non-reentrant cases are furnished by the two cases of de Sitter's world. In the spherical world, as I pointed out in my Note already referred to, the locus of points at infinity consists of two entirely distinct branches, and every world-line meets each branch of the locus once. It is thus clear that we can assign to all the points on one branch the coordinate $s=+\infty$ for all the world-lines on which they lie, and to all on the other branch $s=-\infty$, so obtaining a general distinction between the past and future of every observer. Figs. 5 and 6 make it further obvious that these discriminations are the same for intersecting or paralleloid world-lines.

Fig. 5 shows two intersecting world-lines in which the proper-times are s_1 and s_2, with the section of the light-cone at their point of intersection. Fig. 6 shows two paralleloid world-lines.

Thus in this world the only arbitrary feature is the initial choice which branch of the locus we will call the "Beginning" and which the "End of Eternity."

Fig. 5.

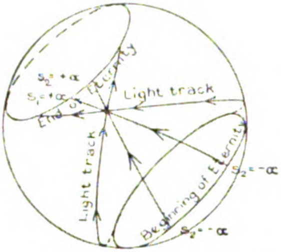
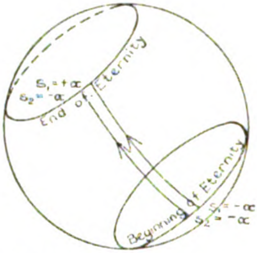
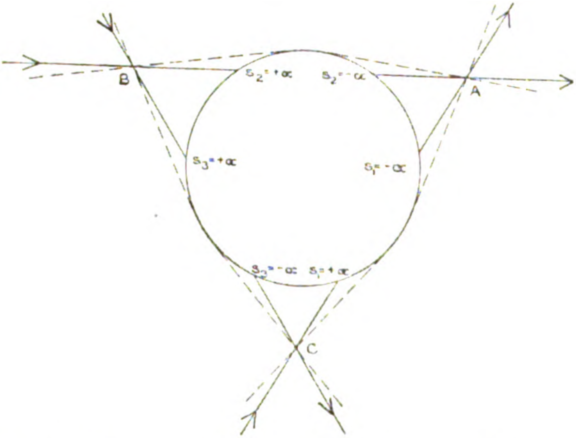


Fig. 6.



In de Sitter's Elliptic world, however, the case is quite different. The locus consists of one branch only and any two points on it whatever may be two points at infinity on a world-line Clearly no general discrimination between past

Fig. 7.



and future is here possible; and we can easily construct three lines intersecting in pairs, such that not all three pairs can possibly be measured in the same sense. Thus in fig. 7—which is in the Cayley-Klein projection—whereas the proper-times s_1, s_2 are measured in the same sense with reference to the intersection A, and s_2 and s_3 are all in the same sense with reference to B, s_3 and s_1 are in opposite senses with reference to C.

Before, however, we utterly reject the elliptic world (which, to me at least, seems to have in other respects decided advantages over the spherical) as a description of actual phenomena, we shall do well to remember that neither claims to be more than a first approximation, and that the sameness of sense of the inhabitants of the earth may perhaps be explained in terms of the departures from de Sitter's metric, which constitute the matter of the world. For instance, the world-lines of all the objects which compose the Earth, including the bodies of sentient observers on its surface, form a sort of rope of myriads of strands, indefinite (probably infinite) in length and roughly constant in thickness, twisted (since the Earth as a whole rotates) and matted—on the surface at any rate—to an indescribable complexity. Now the diameter of the tubular region containing this rope is very small indeed compared with even so much of its length as is known to us (using 1 sec. = 3×10^{10} cm. as basis of comparison), and is also very small compared with the radius of curvature of the world; so that all the world-lines are paralleloid, and (at any rate throughout the known history of the Earth) sameness of sense between them is definable and transitive, just as in the spherical world. This arrangement is clearly conditioned by the structure of the world, since the uniformly small thickness of the rope, and its non-confusion with other world-lines, depend on the law of gravitation, itself an expression of an aspect of the metrical constitution of the world.

An equally elementary instance of a world with re-entrant world-lines is offered by one remarkably similar to de Sitter's. It is interesting as being the only (3 + 1)-dimensional world besides those of de Sitter and Minkowski which is discussible in terms of projective geometry by the introduction of a quadric "absolute." Like de Sitter's world, the absolute divides it into two fields, one only of which is (3 + 1)-dimensional. Taking Wierstrassian coordinates x_1, x_2, y_1, y_2, y_3, we have for the absolute

$$\Sigma(x^2) = \Sigma(y^2),$$

and the (3 + 1)-dimensional field (which we may call actual) is that in which

$$\Sigma(x^2) > \Sigma(y^2).$$

The most convenient restriction is thus

$$\Sigma(x^2) - \Sigma(y^2) = 1,$$

which is satisfied by the values (in terms of four parameters)

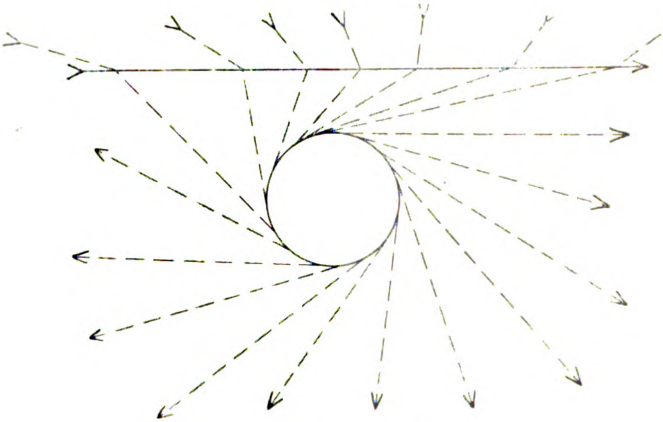
$$\begin{aligned}x_1 &= \cosh\chi\cos t,\\ x_2 &= \cosh\chi\sin t,\\ y_1 &= \sinh\chi\cos\theta,\\ y_2 &= \sinh\chi\cos\theta\cos\phi,\\ y_3 &= \sinh\chi\cos\theta\sin\phi.\end{aligned}$$

The element of length is given (in "natural" units) by

$$\begin{aligned}ds^2 &= \Sigma(dx^2) - \Sigma(dy^2)\\ &= \cosh^2\chi\, dt^2 - [d\chi^2 + \sinh^2\chi(d\theta^2 + \sin^2\theta d\phi^2)]\end{aligned}$$

The negative portion of this is the ordinary 3-dimensional hyperbolic metric; thus the instantaneous space is hyperbolic; time, however, as shown by the values of x_1, x_2, is re-entrant, every world-line having the finite length π or 2π according as we choose the elliptic or spherical case. Thus the absolute encloses the world as a re-entrant sheath rather like the "anchor-ring," the (3+1)-dimensional world corresponding to the region within the ring, and any world-line to a closed curve threaded right round the ring.

Fig. 8.

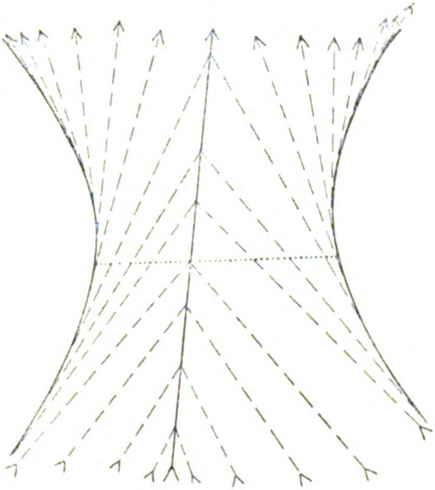


In this illustration we see that it is permissible to speak of a sense this way or that round the ring as a whole, and that two world-lines have determinately the same or opposite senses. Figs. 8 and 9 show an observer's world-line, the fore-cone at all points, and the absolute, in a two-dimensional section, such as $\theta=\phi=0$, so projected that the absolute becomes an ellipse in the one case and an hyperbola in the other.

These figures make clear the continuity of sense of the light-tracks (*cf.* fig. 5 in my Note on de Sitter's world).

Now let us give the world a fictitious beginning, and end by slicing it across along an instantaneous space (t=const.), as shown by the dotted line in fig. 9. This flat space has two distinct faces (corresponding to the two faces of a plane in the three-dimensional geometry); one face contains the "beginning" of the world-line, and the "beginnings" also of all the light-tracks which meet it, the other contains all the corresponding "ends." Thus we can with perfect consistency make the "beginnings" of all world-lines and all light-tracks lie in the one face, and their "ends" all in the other; which leaves sameness of sense determinate and transitive.

Fig. 9.



As (so far as I know) this world has not before been publicly discussed, it may be worth pointing out that most of its properties can be derived from de Sitter's world by a simple imaginary substitution. Real values of the coordinates (t, χ, θ, ϕ) can be assigned to every point; as in de Sitter's world $t =$ const. are flat spaces, but they intersect in a plane in the ideal field (beyond the absolute) so that there is no horizon; $\chi =$ const. are quadrics tending towards the absolute as χ approaches ∞. Motion under the cosmic force is periodic and isochronous, in accordance with the re-entrant character of the time-axis, but (as Prof. Eddington has pointed out to me) the isochronous property is destroyed by the introduction of gravitating bodies, so that it is unlikely that this world will prove of value as a hypothetical approximation to the actual one.

These three worlds have been discussed at perhaps unnecessary length, as instances of the way in which the problem may be approached; what has already been said is, I hope, enough to draw attention to this important question of the sense of time, which seems to me to demand very close investigation, both by the geometer and by the philosopher.

XL. *A Note on Dr. Turner's Paper "Quantum Defect and Atomic Number."*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I SHALL be glad if you will allow me to make some comments on a paper by Dr. L. A. Turner with the above title, which appeared in the September number of the 'Philosophical Magazine.' In this paper Dr. Turner proposes an alteration of the assignment of principal quantum numbers to certain terms of atomic number greater than 28. My object is to show that his reasons for the change hardly seem adequate, and to point out an objection to his scheme of quantum numbers and some quantitative evidence which seems definitely to favour Bohr's assignment, and which has not, so far as I know, been pointed out before.

The principal facts are as follows:—We are concerned only with terms corresponding to orbits which penetrate into the core*. For any atom, let q_0 be the limiting quantum defect for a sequence of terms; we consider the values of q_0 for corresponding sequences of such terms, of atoms of the same chemical subgroup in the same state of ionization (for example, the limiting quantum defects q_0 of the s sequences of neutral Li, Na, K, Rb, Cs).

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* I use the nomenclature *core* and *series electron* for Dr. Turner's *kernel* and *valency electron*; *kernel* tends to be confused with the German *kern* (= nucleus); and in many cases (*e.g.* spectra of highly-ionized atoms) the term *valency electron* for the electron concerned in the emission of the optical series spectrum is somewhat a misnomer. Following Hicks, a set of terms corresponding to orbits with the same value of k but different values of n will be called a *sequence*. *Corresponding sequences* of different atoms are sequences with the same value of k.

If p is the number of the period in the periodic table to which the element belongs, then with Bohr's assignment of quantum numbers, such values of q_0 are approximately linear in p, as pointed out by Prof. H. N. Russell *, and in fact increase by nearly 1 (usually by rather less) for each increase of 1 in p. So that, if q_0 is plotted against the atomic number N, the points lie approximately on a series of straight lines meeting one another at definite angles at points where the difference of N for unit difference of p changes from 8 to 18, or 18 to 32.

On the other hand, Dr. Turner shows that an assignment of quantum numbers can be found such that q_0 is approximately linear in the atomic number N ; and he believes this result to be significant.

None of the linear relations are exact with either assignment of quantum numbers, and Dr. Turner agrees that the fit to his linear relations is no better than that to Russell's relations ; so that no argument as to the significance of either assignment can be obtained from such considerations. He gives four reasons in support of his proposed change, as follows :—

(1) It would be expected that the relation between the values of q_0 and the atomic number N (for corresponding sequences of atoms of the same subgroup) would be represented by some "smooth" curve, rather than a curve made up of pieces of straight lines of different slope.

(2) If there were breaks in the curve due to change of structure in the long periods of the periodic table, such a break would not be expected to occur at potassium (as it does with Bohr's quantum numbers), as the K atom must have one structure or the other, but not both.

(3) If Bohr's quantum numbers were correct, the linear relation between q_0 and N obtained by increasing the quantum numbers (and so the values of q) for Rb and Cs by integers 1 and 2 respectively would be a remarkable coincidence.

(4) Similar alterations give similar results for the different subgroups of the periodic table.

First, I would point out that a reason corresponding to (3) can be framed in support of Bohr's assignment of quantum numbers, viz. :—If Dr. Turner's quantum numbers

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* This observation of Prof. Russell's is quoted (expressed in a slightly different way from that which I have given it here) in a note to Dr. Turner's paper.

were correct, the linear relation between q_0 and p obtained by decreasing the quantum numbers for Rb and Cs by integers 1 and 2 respectively would be a remarkable coincidence*. Apart from an independent idea of the way in which q_0 would be expected to vary with atomic number, such an argument cannot therefore be used in support of either assignment; and the same applies to Dr. Turner's fourth reason.

In connexion with his first reason for the assignment of quantum numbers, Dr. Turner gives no arguments in support of his expectation that the relation between q_0 and N should be represented as a "smooth" curve †; perhaps this is taken as self-evident, but I propose to show that on Bohr's theory it is unjustified.

Before doing this, it may be as well to point out that the quantum defect for a given orbit of the series electron depends in no very simple way on the dimensions of the different groups of orbits in the core and on the numbers of electrons in them; so that when we consider different atoms in the same state of ionization, for which both dimensions of core orbits and number of electrons in them are different, it is not easy to see without quantitative investigation how the quantum defects for corresponding orbits of such atoms will be related. For this reason, ideas of how the quantum defect should vary with atomic number, which are based more or less on guesswork or on purely verbal arguments, may not be very reliable. Nevertheless it is possible to show without mathematics that the values of q_0 given by Bohr's assignment of quantum numbers are consistent with his theory of the structure of the core, and that the facts do not demand the alteration of quantum numbers suggested by Dr. Turner. It is necessary to use one result based on a mathematical investigation—namely, that the smaller the dimensions of a group of core orbits, the smaller its contribution to the quantum defect ‡.

It is easiest to take a definite example, and I will consider

* The two "coincidences" are, of course, not independent: they are connected by the facts that (*a*) the numbers 8, 18, 32, which occur as the differences between atomic numbers of homologous elements, are nearly in the ratio of 1 : 2 : 4; (*b*) that q_0 (Bohr's value) increases by nearly 1 from one such element to the next; and (*c*) that both linear relations are only approximate.

† It is perhaps as well to point out that, either for the elements of a subgroup or for all the elements, q_0 is a function of a discontinuous variable N; so that to speak of a "continuous" variation of q_0 with N is meaningless. If q_0 is plotted against N and a curve drawn through the points for a given subgroup, it must be remembered that apart from the plotted points this curve is purely diagrammatic, and that intermediate points on the curve have no physical significance.

‡ This result can easily be seen from some theoretical work which I have given elsewhere (Proc. Roy. Soc. vol. 106. p. 552 (1924)).

the *s* sequences of the alkali metals. From Li to K the difference of atomic number is 16, and the increase of q_0 is nearly 2. From K to Rb the atomic number increases by 18; so, according to Dr. Turner, the limiting quantum defect would be expected to increase by about 2 again. This might perhaps be the case if the difference of structure between K and Rb were comparable to the difference of structure between Li and K; but this is not so, as shown by the fact that the difference of atomic number between K and Rb is 18 and not 16, and by the absence of an element with atomic number and properties intermediate between K and Rb corresponding to Na between Li and K.

By going into some details, we can deduce the direction in which the actual value of q_0 for Rb should differ from the value extrapolated from the relation between q_0 and N for Li, Na, and K.

The core of the Li atom consists of two orbits of principal quantum number $n=1$; the core of the K atom consists, in addition, of 8 orbits with $n=2$ which lie well outside * the orbits with $n=1$, and a group of 8 orbits with $n=3$ which similarly lie well outside the orbits with $n=2$.

Let us imagine an atom of the atomic number of Rb, whose difference in structure from the K atom is comparable to the difference between thisand the Li atom; that is, imagine an atom with a core built up of an argon-like structure similar to the core of a K atom, with another group of electrons (say 9) *outside* it and a further group of electrons (say 9) *outside* that. I will call this a "pseudo-Rb" atom. We might perhaps expect that the relation between q_0 and N for Li, Na, K, and pseudo-Rb would be represented by a smooth curve. But on Bohr's theory 10 of the 18 electrons which have to be added to the argon-like structure to give the core of the Rb atom are in orbits of the same principal quantum number, and so of the same dimensions, as some orbits already present. The consequence is that the dimensions both of the orbits of these 10 electrons, and of the orbits of the further 8 electrons, are smaller than they would be if all the 18 electrons were added in orbits outside the argon-like structure as in the case of pseudo-Rb. The result of this is that the quantum defect for any orbit of the series electron which penetrates into the core must be considerably smaller than it would be for pseudo-Rb;

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* Some of the orbits of the group of principal quantum number 2 penetrate into the region in which those of quantum number 1 move; in saying that one orbit lies "outside" another, I mean only that its time mean radius is greater.

i. e., smaller than the quantum defect extrapolated from the relation between q_0 and N for Li, Na, and K.

This is in complete agreement with observation, if Bohr's assignment of quantum numbers is adopted. On the other hand, if Dr. Turner's quantum numbers are adopted, the value of q_0 for Rb lies somewhat *above* a reasonable smooth (q_0, N) curve passing through the points for Li, Na, and K (the curve not being restricted to be a straight line).

Similar reasoning shows that the value of q_0 for the *s* sequence of Cu must be *smaller* than the value obtained by extrapolating the relation between q_0 and N for Li, Na, and K; this is the case if Bohr's quantum numbers are adopted, but Dr. Turner's quantum numbers bring the Cu point above the curve for the alkali metals.

Also, in contradiction to Dr. Turner's second reason for his assignment of quantum numbers, it appears, according to the above reasoning, that a break of the (q_0, N) curve for the alkali metals would be expected just at potassium, since it is the element of the subgroup before and after which the process of building up the atom is different.

It seems, therefore, that the facts called by Dr. Turner in evidence of his proposed alteration of quantum numbers are in no way inconsistent with Bohr's theory of the core structure and his assignment of quantum numbers to orbits of the series electron. I will now turn to an objection to Dr. Turner's scheme, and some positive evidence in favour of Bohr's scheme.

The former can best be explained by an example. If for Cs the first *s* term of the optical spectrum corresponds to an 8_1 orbit (Dr. Turner's assignment) instead of a 6_1 orbit (Bohr's assignment), what are we to think of the 6_1 and 7_1 orbits, which must be more firmly bound than the 8_1? They cannot be possible orbits of the series electron, since the orbit corresponding to the first *s* term is the normal, and so most firmly bound, orbit of the series electron, as shown by the ready absorption of the principal series, and by the agreement of the ionization potential with the value of the term. If terms corresponding to the 6_1 and 7_1 (and 6_2 and 7_2) orbits do not appear in the optical spectrum, it must be because the core already contains electrons in these orbits; if so, terms corresponding to them would be expected to appear in the X-ray spectrum, and such terms would be expected to be quite fairly large for the heavier elements for which Dr. Turner's assignment of quantum numbers to orbits of the series electron demands 9_1 and 10_1 core orbits. Actually, if the usual classification of X-ray terms is accepted, P X-ray terms $(n=6)$ only appear in the very heaviest elements, in accordance with Bohr's assignment of quantum numbers, and there seems no reason at all to upset this classification.

Finally, I will mention some positive evidence for Bohr's assignment of quantum numbers to orbits of the series electron.

The wave-numbers of the first *s* or *p* terms of the spectra of different elements of the same subgroup are not far different, the general (but not universal) tendency being for the wave-number to increase somewhat with decreasing atomic number; with Bohr's assignment the principal quantum number of the orbit in question increases by 1 from one period to the next. Examples are given in Table I.

TABLE I.—Orbits of Series Electrons.

Element.	N.	Orbit.	ν/R.
Cs	55	6_1	·286
Rb	37	5_1	·307
K	19	4_1	·319
Na	11	3_1	·376
Li	3	2_1	·396
Au	79	5_1	·679
Ag	47	4_1	·557
Cu	29	3_1	·568

Values for ν/R from Fowler's 'Report on Series in Line Spectra,' except for Au, for which the term value is taken from a paper by Thorsen (*Naturwiss.* vol. xxvii. p. 501, 1923).

TABLE II.—Core Orbits.

Element.	N.	Orbit.	ν/R.	Orbit.	ν/R.
Th	90	5_1	19·8	5_2	about 11
Ce	58	4_1	21·7	4_2	15·8
Z	40	3_1	31·4	3_2	(25)
Pb	82	5_1	10·3	5_2	6·4
Sn	50	4_1	10·7	4_2	6·6
Ge	32	3_1	(12·9)	3_2	[9·0]
Au	79	5_1	7·8	5_2	8·3 ? [3·8]
Ag	47	4_1	7·5	4_2	3·3 ? [3·9]
Cu	29	3_1	(8·3)	3_2	5.2
Cs	55	5_1	(2·2)		
Rb	37	4_1	(2·4)		
K	19	3_1	(3·0)		
Na	11	2_1	(4·0)		

Values not bracketed have been taken from a paper by Coster (*Naturwiss.* vol. xxvii. p. 567); values in brackets have been obtained by reading off curves of ν/R against N, given in diagrams in this paper—those in square brackets from interpolated parts, and those in round brackets from extrapolated parts of these curves. The value for the 5_2 orbit of Th is interpolated from Coster's table: the value $\nu/R=17$ obtained by reading off the curve seems unlikely.

There is a corresponding relation between the X-ray spectra of such elements which I have not seen pointed out hitherto. If we consider terms corresponding to loosely-bound n_k core orbits of elements of the same subgroup, keeping k constant but increasing n by 1 on going from one period to the next, it is found that these terms also are not far different, and show a general tendency to increase with decreasing atomic number. Examples are given in Table II.

A mathematical analysis on the assumption of a central field shows that this correspondence is significant, and that if for elements of the same subgroup the values of the terms corresponding to loosely-bound core orbits with a given value of k, but values of n increasing by 1 from one period to the next, are nearly the same, then, if the orbits of the series electron for that value of k penetrate into the core, the value of q_0 for them must increase by about 1 from one period to another of the periodic table.

Table II. shows that the values of such X-ray terms are in fact nearly the same, and the conclusion gives an almost decisive preference to Bohr's quantum numbers for the orbits of the series electron.

Further evidence is given by a detailed numerical analysis of the field of the atom from the observed terms of the optical and X-ray spectra on lines worked out independently by Fues* and myself†. Fues (*loc. cit.* 4th paper) has shown that for Cs, assuming Bohr's quantum numbers, a central field can be found which will reproduce the observed terms of the optical and X-ray spectra with errors not much greater than those for Na, Mg^+, and Al^{++}. I have come independently to the same conclusion, and in fact have found it possible in the case of Rb and Cs to determine the atomic field approximately without making use of the s and p terms of the optical spectra; from the field so found, the quantum defects for these terms can be calculated, and most definitely confirm Bohr's assignment of quantum numbers, and not Dr. Turner's.

I conclude, therefore, that not only is there no demand for the alteration of quantum numbers suggested by Dr. Turner, but further that, at any rate in most cases, Bohr's quantum numbers for terms corresponding to those orbits which penetrate the core are definitely correct.

St. John's College,
Cambridge.

Yours faithfully,
D. R. HARTREE.

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* E. Fues, *Zeit. f. Phys.* vol. ii. p. 364, vol. xii. p. 1 (1922); vol. xiii. p. 211 (1924); vol. xxi. p. 265 (1924).

† D. R. Hartree, Proc. Camb. Phil. Soc. vol. xxi. p. 625 (1923).

XLI. *The Magnetic Rotary Dispersion of certain Paramagnetic Solutions.* *By* R. W. Roberts, *M.Sc., Asst. Lecturer and Demonstrator in Physics, The University of Liverpool* [*].

In a previous paper [†] on this subject it was shown that, in solutions of cobalt sulphate and cobalt acetate in water, the cobalt atom is capable of producing a negative magnetic rotation. This rotation, although large relative to water, appeared only on the high-frequency side of the principal absorption-band which lies at the borders of the visible and ultraviolet. In an aqueous solution of cobalt chloride the rotation was nowhere negative, although from the form of the rotary-dispersion graph of this solution it was evident that, on the ultraviolet side of the absorption-band, the cobalt atom was exerting a negative rotation. In solutions of the corresponding salts of nickel, no trace of a negative rotation was apparent.

In view of these results, which do not seem to have a ready explanation on the modern theory of magneto-optics, it seemed worth while to continue the investigations with solutions of other cobalt and nickel salts. For the purpose of calculation, the refractive indices of these solutions in the visible and ultraviolet have also been determined, and an endeavour has been made to enter into a quantitative examination of the experimental results.

In the work previously published, owing to the lack of a suitable source of light, the rotation for only one wave-length could be found on the visible side of the absorption-band in the cobalt solutions. Using a mercury vacuum lamp, and by working with more dilute solutions, it was found that the rotary dispersion in the neighbourhood of the absorption-band was strongly anomalous.

The presence of anomalous rotary dispersion, as we here use the term, is not predicted by the usual magneto-optical theory based on the Hall effect, yet instances of absorption-bands exhibiting anomalous rotary dispersion are not wanting. Schmauss [‡] found that anomalous rotary dispersion existed in alcoholic solutions of the aniline dyes; his results, however, were not confirmed by Bates [§]. Livens [||] has shown that Schmauss's results can be explained on the hypothesis of the Hall effect, when allowance is made for the polarization of the medium due to the electric force of the light wave. Schmauss[*] has also found instances of anomalous rotary dispersion in liquid oxygen and in aqueous solutions of neodymium, praseodymium, and erbium nitrate. These results have been confirmed in part by the researches of G. J. Elias[†], who found distinct examples of anomalous rotation in some solutions of the rare earths. Unmistakable evidences of anomalous rotary dispersion have been found by R. W. Wood[‡] in an aqueous solution of praseodymium nitrate and in a solid film of neodymium nitrate. At the temperature of liquid air, J. Becquerel[§] found the crystals tysonite and xenotime to possess anomalous rotation. It is noteworthy that in all the cases cited, with the exception of the alcoholic solutions of the aniline dyes, the substances are paramagnetic. It appears, therefore, that the study of the magnetic rotary dispersion in paramagnetic substances is capable of yielding information which cannot be obtained from the study of ordinary dispersion alone[‖].

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[*] Communicated by Prof. L. R. Wilberforce, M.A.

[†] Richardson, Roberts, and Smith, Phil. Mag. xliv. p. 912 (1922).

[‡] *Ann. d. Phys.* ii. p. 280 (1900).

[§] *Ann. d. Phys.* xii. p. 1091 (1903).

[||] Phil. Mag. xxvi. p. 362 (1913).

ROTARY DISPERSION FORMULÆ.

Most of the rotary dispersion formulæ have been based on the generalized Sellmeier formula,

$$n^2 = a_0 + \frac{a_1}{\lambda^2 - \lambda_1{}^2} + \frac{a_2}{\lambda^2 - \lambda_2{}^2} + \ldots\ldots$$

A better basis would be the Lorenz-Lorentz formula,

$$\frac{n^2 - 1}{n^2 + 2} = a_0 + \frac{a_1}{\lambda^2 - \lambda_1{}^2} + \frac{a_2}{\lambda^2 - \lambda_2{}^2} + \ldots\ldots$$

Certainly, in work on dispersion—particularly in the case of solutions—the Lorenz-Lorentz formula gives a far better representation of the experimental facts than the Sellmeier formula does. Using the Lorenz-Lorentz formula, an expression for the magnetic rotation of a substance may be easily derived. Larmor[¶] has shown that, in the case of a substance whose vibrators are subjected to the Hall effect and have all the same value for $\frac{e}{m}$, the magnetic rotation δ is given by the formula (of the Becquerel type),

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[*] *Ann. d. Phys.* x. p. 853 (1903).

[†] *Ann. d. Phys.* xxxv. p. 299 (1913).

[‡] Phil. Mag. ix. p. 725 (1905); xv. p. 270 (1908).

[§] Phil. Mag. xvi. p. 153 (1908).

[‖] *Cf.* J. J. Thomson, Phil. Mag. xl. p. 713 (1920).

[¶] 'Æther and Matter,' p. 352.

$$\delta = -\frac{e}{2mc^2}\lambda\frac{dn}{d\lambda}, \quad . \quad . \quad , \quad . \quad . \quad (1)$$

where e is the electronic charge in electrostatic units.

The Lorentz formula may be written in the form *

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3}\Sigma\frac{e^2}{m(p_s^2-p^2)}, \quad . \quad . \quad . \quad . \quad (2)$$

in which symmetrical units are used as in (1) and the suffix to them has been dropped.

We have therefore

$$\frac{3}{n^2+2} = \text{const.} - \frac{e^2}{3\pi mc^2}\Sigma\frac{\lambda_s^4}{\lambda_2-\lambda_s^2}. \quad . \quad . \quad . \quad (3)$$

Using (1) and (3), we obtain

$$\delta = \frac{e^3}{18\pi m^2c^4}\cdot\frac{(n^2+2)^2}{n}\Sigma\frac{\lambda_s^4\lambda^2}{(\lambda^2-\lambda_s^2)^2}. \quad . \quad . \quad . \quad (4)$$

which is a simple deduction of the polarization formula obtained by Sir J. Larmor †, S. S. Richardson ‡, and L. H. Siertsema §. For solutions we shall use (4) in the form

$$\frac{\delta\lambda^2 n}{(n^2+2)^2} = x\frac{\delta_w\lambda^2 n_w}{(n_w^2+2)^2} + \Sigma\frac{a_s}{(1-\lambda^{-2}\lambda_s^2)^2}, \quad . \quad . \quad (5)$$

where n, n_w are the refractive indices of the solution and solvent respectively, and δ, δ_w the corresponding rotations; x is the number expressing the mass in gm. of solvent in 1 c.c. of the solution. The a_s's are quantities involving electronic constants, and the λ_s's are the characteristic wave-lengths of the solute. For colourless solutions, Heydweiller ‖ and his co-workers have shown that the natural dispersion in the visible and ultraviolet is controlled by a number of electrons belonging to the anion of the dissolved salt and a comparatively larger number of electrons of

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* O. W. Richardson, 'The Electron Theory of Matter,' p. 148.

† 'Æther and Matter,' p. 200.

‡ Phil. Mag. xxxi. p. 454 (1916).

§ Proc. Amst. Acad. xviii. 2, p. 925.

‖ *Ann. d. Phys.* xli. p. 499 (1913); xliv. p. 977 (1914); xlix. p. 653 (1916).

much higher frequency. The free period of the anion electrons controlling the dispersion appears to be almost independent of the kation. For coloured solutions, one or more additional λ_s's must be introduced.

If we form the difference

$$\Delta = \frac{\delta\lambda^2 n}{(n^2+2)^2} - x\frac{\delta_w\lambda^2 n_w}{(n_w^2+2)^2}$$

from the experimental results, we may take

$$\Delta = \Sigma\frac{a_s}{(1-\lambda^{-2}\lambda_s^2)^2}$$

to be that additive quantity on the basis of the Hall effect hypothesis which is characteristic of the solute. The differences Δ for the salts used in the present work have been plotted against λ^{-2} in fig. 6. It will be readily seen from the strong anomalous rotary dispersion at the absorption-bands, that the hypothesis of the Hall effect alone cannot explain the experimental results.

Drude * has developed a formula on the hypothesis of molecular currents which predicts the possibility of anomalous rotary dispersion. It is most likely that in the paramagnetic liquids under consideration both the molecular currents and the Hall effect are operative. As a first approximation we shall consider only the molecular current effect, and on this hypothesis we shall obtain a further polarization formula. The following analysis is a modified form of that due to Drude, taking into account the force arising from the polarization of the medium, which force Drude neglects. Only the leading steps in the working are given, and for the sake of brevity and simplicity quaternion notation is used. Where the symbols are given without definition they are to be taken as having the meaning given by Drude.

Consider a plane polarized wave travelling in the direction of the magnetic field. Let this direction coincide with the z axis which is parallel to the unit vector k.

Maxwell's equations for the medium may be written

$$\frac{1}{c}\frac{\partial}{\partial t}(\mathbf{H} + V\nabla\Sigma\xi_s\alpha_s) = -V\nabla\mathbf{E}, \quad . \quad . \quad . \quad (6)$$

$$\frac{1}{c}\frac{\partial\mathbf{D}}{\partial t} = V\nabla\mathbf{H}, \quad . \quad . \quad . \quad (7)$$

where

$$\alpha_s = 4\pi\frac{N_s e q_s}{c T_s}k,$$

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* Drude, 'Theory of Optics,' p. 418.

and ξ_s is the displacement of the centre of the orbit of the revolving electron of type s.

The equation of motion of this centre is

$$m_s\ddot{\xi}_s = -k_s\xi_s + e\left(\mathbf{E}+\frac{4\pi}{3}\mathbf{P}\right).$$

If $\xi_s \propto e^{ipt}$ we have, in the usual way,

$$\xi_s = \frac{e\mathbf{E}}{m_s(p_s^2-p^2)} \cdot \frac{1}{1-\frac{4\pi}{3}\Sigma\frac{e^2}{m_s(p_s^2-p^2)}},$$

which, by eqn. (2), gives

$$\xi_s = \frac{(n^2+2)}{3}\,\frac{e\mathbf{E}}{m_s(p_s^2-p^2)}.$$

Remembering that $\nabla = k\frac{\partial}{\partial z}$, and taking $\mathbf{E}=\mathbf{E}_0 e^{ip\left(t-\frac{z}{v}\right)}$ with $\mathrm{S}k\mathbf{E}_0=0$, we have, following the convenient procedure of Leigh Page *, the two equations

$$\frac{\partial^2\mathbf{E}_0}{\partial z^2} = 2\frac{p}{v}\,\mathrm{C}_p\mathrm{V}k\frac{\partial\mathbf{E}_0}{\partial z} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and

$$\frac{2p}{v}\,\frac{\partial\mathbf{E}_0}{\partial z} = -\mathrm{C}_p\mathrm{V}k\frac{\partial^2\mathbf{E}_0}{\partial z^2} + \frac{p^2}{v^2}\mathrm{C}_p\mathrm{V}k\mathbf{E}_0. \quad . \quad . \quad (9)$$

where

$$\mathrm{C}_p = \frac{4\pi}{3c^2}(n^2+2)\,.\,\Sigma\,\mathrm{N}_s\frac{e^2q_s}{m_s\mathrm{T}_s}\,\frac{p}{p_s^2-p^2},$$

which are obtained from (6) and (7) by eliminating **H**, and separating out the real and imaginary parts.

Neglecting the square of C_p, we obtain

$$\frac{\partial\mathbf{E}_0}{\partial z} = \frac{p}{2v}\mathrm{C}_p\mathrm{V}k\mathbf{E}_0$$

$$= \frac{2\pi}{3c^3}n(n^2+2)\,\Sigma\,\mathrm{N}_s\frac{e^2q_s}{m_s\mathrm{T}_s}\,\frac{p^2}{p_s^2-p^2}\mathrm{V}k\mathbf{E}_0,$$

which gives the rotation per cm.

$$\delta = \frac{2\pi}{3c^3}n(n^2+2)\,.\,\Sigma\,\mathrm{N}_s\frac{e^2q_s}{m_s\mathrm{T}_s}\,\frac{\lambda_s^2}{\lambda^2-\lambda_s^2}.$$

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* 'An Introduction to Electrodynamics,' p. 128.

We shall use this equation in the form

$$\frac{\delta\lambda^2}{n(n^2+2)} = x\frac{\delta_w\lambda^2}{n_w(n_w^2+2)} + \Sigma\frac{a_s}{1-\lambda^{-2}\lambda_s^2}, \quad . \quad . \quad (10)$$

where the a_s's are quantities involving electronic and orbital constants (for a given field), and the remaining symbols have the same meaning as in eqn. (5). Drude's formula (38) p. 431, is obtained from (10) by taking $n^2+2=$constant, $x=0$, and $\lambda_s=\lambda_1$ and 0.

Forming the difference

$$D = \frac{\delta\lambda^2}{n(n^2+2)} - x\frac{\delta_w\lambda^2}{n_w(n_w^2+2)},$$

which may be calculated from the experimental results, we obtain a quantity which is characteristic of the solute. The differences D for the salts used in the present work are given in graphical form in fig. 5. As with the Δ differences, we get anomalous dispersion at the absorption-band with the D differences. The formula for the D difference is able, however, to account for this anomalous dispersion, not only qualitatively but, as we shall see later, quantitatively. The best dispersion formula is that which will enable us to calculate the position of the absorption-bands in the spectrum, and at the same time to be able to account for the dispersion with the minimum number of constants. For the cobalt solutions considered, we shall see later that equation (10) is able to give a good approximate value for the wave-length of the principal absorption-band and also a representation of the rotary dispersion graphs almost within the limits of experimental error. It may be mentioned in passing that S. S. Richardson [*] has given a rotary dispersion formula with few constants by means of which the absorption-bands and rotary dispersion of certain diamagnetic liquids can be calculated with extremely good accuracy. The formula is based on the Hall effect hypothesis.

EXPERIMENTAL.

Magnetic Rotation.

The method was the same as that described briefly in the previous paper. Owing to the strong absorbing power of the solutions, exposures of ten to twelve minutes' duration were necessary. To keep the work within reasonable limits, the readings obtained from the pilot plates have all been used in the construction of the graphs. For very strong lines the actual settings of the analyser were determined which gave equality of illumination of the lines in the upper and lower spectra of the divided field. About a dozen exposures were made on each plate—the first, third, etc. giving "half-shades" with the field in one direction, the second, fourth, etc. with the field in the opposite direction. The distances of the lines at which the "half-shades" occur from some well-known line in the iron arc spectrum were determined, and by means of a calibration curve, which was found to fit all the spectrograms with good accuracy, the wave-lengths of the "half-shade" lines were obtained. A graph was drawn in which the setting of the analyser was plotted against the half-shade wave-length. In the upper half of this graph the points refer to the settings with the field in one direction, and in the lower half to those obtained with the field in the opposite direction. From this graph could be found the doubled rotation for any wave-length well within the extreme half-shade wave-lengths. When this method was adopted, the rotations for wave-lengths ·4, ·38, ·36, ·34 μ, etc. were found, and these rotations were used in the construction of the rotary dispersion gr phs. From the dozen points provided by each pilot plate, the rotations for two of the above-mentioned wave-lengths were obtained. It was arranged that one of these wave-lengths was included in the range of "half-shade" wave-lengths taken in by the next pilot plate. The agreement between the rotations obtained from different plates for the common wave-lengths was good. As a further check on the accuracy of this procedure, the rotations for a few of the strongest lines in the vacuum arc mercury spectrum were observed for some of the solutions; and it will be seen from the graphs that the rotations obtained in this way are quite close to the curve determined by the above method. It is extremely important for work in the near ultraviolet that the solutions should be as clear and pure as possible. Although the presence of small traces of impurities does not affect the rotation appreciably, it does, to a marked degree, affect the absorption. This was particularly noticeable with several of the nickel solutions investigated. For these salts, there is only a very narrow transparent region in the ultraviolet on the short wave-length side of the absorption-band at ·405 μ [*]. Repeated filtering in several cases gave a great improvement in the intensity of the spectrograms. To reduce the rotations to absolute measure, Rodger and Watson's value * for Verdet's constant of water at 20° C. for the yellow sodium line, namely 0·01309 min. per cm.-gauss, was used. The water-curves in figs. 1–4 have been constructed from the ratio values for the rotation of some strong lines in the iron arc spectrum given by S. S. Richardson †, using the above-mentioned Verdet's constant and the results of a large number of observations of the rotation of water for the sodium line 5893 and the iron line 4958. The curve obtained in this way was checked by direct determinations of the rotations for the mercury lines 5461, 4358, and the iron line 3306.

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[*] Phil. Mag. xxxi. p. 232 (1916).

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[*] Houstoun, Proc. Roy. Soc. Edin. xxxi. p. 547 (1911).

For all the rotations the correction for the end plates of the cell containing the liquids under test has been made by calculation, on the assumption that the rotation of the end plates varied as λ^{-2}. This assumption is a sufficiently accurate one, especially so in the formation of the differences D and Δ.

Refractive Indices.

As far as the author is aware, the determination of the refractive indices in the ultraviolet of aqueous solutions of nickel and cobalt salts, with the exception of nickel chloride‡, does not seem to have been made. In the visible spectrum, however, Limann § has determined the refractive indices of aqueous solutions of a few nickel and cobalt salts for the lines H_α, Na ·5893 μ, H_β, and H_γ.

The refractive indices of the solutions used in the present work were determined very simply and rapidly in the following way. The ordinary glass lenses of a spectrometer were removed, and replaced by two achromatic quartz-fluorite combinations constructed by Hilger. A hollow prism with very nearly plane parallel quartz coverplates was carefully levelled and fixed on to the table of the spectrometer. Instead of the eyepiece, a photographic plate-holder was screwed on to the end of the inner draw-tube of the telescope at right angles to its axis. The spectrometer was adjusted for parallel light by Schuster's method ||, using the iron arc as source and focussing the

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* Phil. Trans. A 186. p. 621 (1895).

† S. S. Richardson, Phil. Mag. xxxi. p. 232 (1916).

‡ Heydweiller u. Grube, *Ann. d. Phys.* xlix. p. 653 (1916).

§ Limann, *Zeit. f. Phys.* viii. p. 13 (1922).

|| Phil. Mag. [5] vii. p. 95.

iron lines ·4046 and ·4068 μ (mean line). The focussing was done on a plain glass plate with fine lines ruled with a diamond on the side of the plate which first received the light. While the adjustments were made, the lines were observed with an eyepiece which was allowed to rest on the plain glass plate. In this way the resulting ultraviolet spectrum was found to be quite sharp throughout the region to be investigated. Instead of the usual wedge covering the slit, a sliding diaphragm with two apertures was employed, which—at a later stage—was replaced by one with three apertures when I found that such diaphragms were in common use.

The prism was first filled with water whose temperature was taken by a thermometer to an accuracy of $0^{\circ}\cdot 1$ C. With the slit exposed to the light of a cadmium spark passing through the upper aperture of the diaphragm, an exposure of one to two minutes was made. The resulting spectrum may be conveniently termed a "water" spectrum. After this exposure, the diaphragm was removed so that the light was cut off from the slit, while the prism was emptied and rinsed out several times with the solution under test. When filled with the solution, a "solution" spectrum was taken with the slit exposed to the light passing through the middle aperture. To make sure that the prism was not moved during the process of emptying and filling, a second "water" spectrum was taken using the lower aperture of the diaphragm. The lines of this spectrum were in every case found to be under the lines of the first "water" spectrum. To vary the conditions of the work somewhat, another set of spectra was obtained on the same plate with the prism in a different position. The spectra were carefully measured to an accuracy of 1/800 mm., and from the measurements the refractive indices of the solution were determined graphically.

Flatow[*] has studied with great care the refractive indices of water in the visible and ultraviolet. From his results, by drawing refractive index-temperature graphs, I find the following refractive indices for water at 13° C. :—

λ.	n.	λ.	n.
·2195	1·39934	·3404	1·35085
·2265	1·39307	·3612	1·34780
·2313	1·38929	·3944	1·34409
·2428	1·38152	·4416	1·34020
·2573	1·37391	·4678	1·33858
·2676	1·36950	·4800	1·33793
·2749	1·36685	·5339	1·33544

[*] *Ann. d. Phys.* xii. p. 85 (1903).

Using these values, a large-scale graph (with *n* plotted against λ) was drawn in three parts with the aid of a curve-tracer. The parts of this graph were made to overlap as much as possible. By means of this graph, the refractive indices of water for any wave-length within the range could be readily determined.

Having determined the refractive indices for a number of known lines in the "water" spectrum, which were chosen so as to be as nearly equally spaced as possible, a graph was drawn with these refractive indices plotted against the scale-readings of the chosen lines. This graph was found to be very nearly linear. Since lines with the same scale-reading have the same refractive index, the refractive indices of the solution for any line in its spectrum could be obtained from the graph when the scale-reading of the line is known.

The refractive indices obtained from the various prism settings agreed well within the limits of experimental error. In the graphs, one unit in the fifth decimal place was represented by one-tenth of a tenth of an inch so that estimates of the fifth decimal place in the refractive index could be made. Most of the results agreed within 8 units in the fifth figure of decimals, and in many cases the agreement was better than this.

The results of the refractive index determinations are given in the form of two graphs. For the magnetic rotation work these results are given to the fourth decimal place. The recorded refractive indices have all been read off from the graphs prepared for figs. 7 & 8, and corrected for the temperature difference from the temperatures neighbouring 13°·0 C. to 20°·0 C. on the assumption that the correction would be the same as that for water. This is sufficiently accurate for the purpose of calculation in the magnetic work. The temperature varied only very slightly during the time the photographs were taken. The mean temperature has been recorded in each case.

Using water as the reference liquid, refractive indices not much higher than 1·39 can be determined. With the present dearth of refractive index determinations for pure liquids in the ultraviolet, some solutions whose refractive indices were in the neighbourhood of 1·40 could not be determined by this method.

In some cases the mercury arc was used as a source instead of the cadmium spark. With such an intense source, the best photographs were obtained by forming an image of the source in the prism. In this way only the central portions of the lenses were used. Preliminary experiments showed that, for the range of refractive indices considered, the error due to the spreading of the lines on the plate arising from the want of achromatism of the camera lens was small.

SOLUTIONS.

The concentrations of the solutions have been determined by electrolytic deposition of the metal (Ni or Co) from ammoniacal solutions. In the case of nickel chlorate and cobalt chlorate solutions, the deposits were excellent. These chlorates were obtained from Kahlbaum. The recorded densities refer to room temperature, at which temperature all the solutions were prepared.

For the cobalt nitrate solution the concentration has been taken from the tables given by Heydweiller[*]. This was necessary owing to loss of the solution through accident.

RESULTS.

Water.

In the formation of the D and Δ differences the functions $\frac{R_w\lambda^2}{n_w(n_w^2+2)}$ and $\frac{R_w\lambda^2 n_w}{(n_w^2+2)^2}$ are repeatedly required. R_w is Verdet's constant in minutes per cm.-gauss. The required values have in all cases been read off from graphs of these functions, constructed with the data given below. The values of n_w for 20° C. have been taken from Flatow's results.

λ.	R_w.	$\frac{R_w\lambda^2\times 10^4}{n_w(n_w^2+2)}$.	$\frac{R_w\lambda^2 n_w\times 10^4}{(n_w^2+2)^2}$.
·5893	·0131	9·030	4·248
·4958	·0190	9·230	4·355
·4529	·0232	9·372	4·430
·4308	·0260	9·465	4·480
·4199	·0275	9·519	4·512
·4046	·0299	9·597	4·550
·3609	·0391$_5$	9·919	4·719
·3100	·0573	10·562	5·070

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[*] *Zeits. f. Anorg. u. Allg. Chem.* cxvi. p. 42 (1921).

Cobalt Solutions.

Cobalt Chlorate. (Fig. 1.)

(i.) Strong solution: density $= d = 1{\cdot}355$ gm. per c.c. $x = {\cdot}875$.

Obs.	λ in μ.	$n_{20°}$.	$R_{(\text{obs.})}$.	$R_{(\text{calc.})}$.	$\delta R \times 10^4$.
a	·5780	1·3911	·0143	·0143	ref.
b	·4358	1·3984	absorpt.	—	—
c	·4046	1·4010	·0231	·0231	ref.
d	·3714	1·4044	·0295	·0295	0
e	·3664	1·4051	·0307	·0307	ref.
f	·3592	1·4060	·0325	·0323	+2
g	·3342	1·4095	·0391	·0393	−2

The absorption of this solution in the neighbourhood of the absorption-band at ·510 μ was so strong that, using a powerful mercury arc, no observations could be made for the strong lines ·5461 and ·4358 μ. With the exception of (*a*), the magnetic observations were obtained photographically. The ultraviolet refractive indices have been obtained by extrapolation from the results of visual observations with a Pulfrich refractometer on the mercury lines ·5780 (mean line), ·5461, ·4358, and ·4046 μ.

If we try to represent the dispersion by means of a two-constant formula for the D difference, we find that, from observations (*a*) and (*c*), $\lambda_1 = {\cdot}448\ \mu$, and from (*c*) and (*e*), $\lambda_1 = 1{\cdot}239\ \mu$.

This indicates that the effect of the high-frequency electrons has been omitted. Providing for these, we take

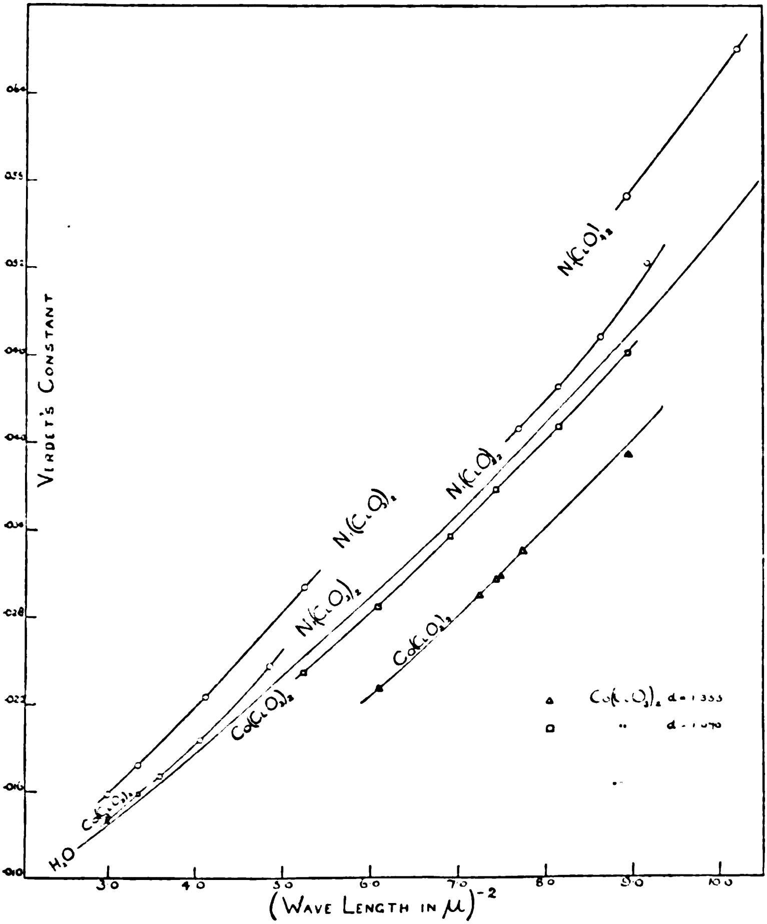
$$D = \frac{a_1}{1 - \lambda^{-2}\lambda_1^2} + a_2.$$

From (*ace*) $\lambda_1 = {\cdot}499\ \mu$, which, considering the simple assumptions which have been made, is a fair approximation to the value $\lambda = {\cdot}510\ \mu$ given by Houstoun for the position of the principal absorption-band. With the value $\lambda = {\cdot}499\ \mu$ we find

$$a_1 = +4{\cdot}07 \times 10^{-5},$$
$$a_2 = -7{\cdot}93 \times 10^{-5}.$$

Using these values, it will be seen that the Verdet's constants calculated from the formula are close to the observed ones.

Fig. 1.



(ii.) **Weak solution** : $d=1{\cdot}070$ gm. per c.c., $x={\cdot}978$.

Obs.	λ in μ.	n_{20}.	$R_{(obs.)}$.	$R_{(calc.)}$.	$\delta R\times 10^4$.
a	·5780	1·3446	·0140	·0138	+2
b	·5461	1·3458	·0159	·0159	ref.
c	·4358	1·3516	·0242	·0242	ref.
d	·4046	1·3541	·0288	·0290	−2
e	·3800	1·3569	·0336	·0337	−1
f	·3664	1·3588	·0368	·0368	ref.
g	·3500	1·3612	·0410	·0411	−0
h	·3342	1·3640	·0462	·0461	+1

As with the strong solution, the position of the absorption-band cannot be calculated from a two-constant formula.

Taking the formula

$$D = \frac{a_1}{1 - \lambda^{-2}\lambda_1^2} + a_2,$$

we find from (acf), $\lambda_1 = \cdot 517\,\mu$,

(bcf), $\lambda_1 = \cdot 507\,\mu$.

Using the latter value for λ_1, we obtain

$$a_1 = +6\cdot 7 \times 10^{-6},$$
$$a_2 = -1\cdot 36 \times 10^{-5}.$$

With these values we find good agreement between the calculated and observed values of R.

It will be observed that with both solutions of $Co(ClO_3)_2$ we have the appearance of a negative constant. Such constants have been attributed to the existence of positive electrons. On Drude's theory, the presence of the negative constants means that the high-frequency electrons contribute to the paramagnetism of the solution.

Cobalt Bromide. (Fig. 2.)

$d = 1\cdot 100$ gm. per c.c., $x = \cdot 990$.

Obs.	λ in μ.	n_{20°	$R_{(obs.)}$	$R_{(calc.)}$	$\delta R \times 10^4$.
a	·5893	1·3520	·0151	·0149	+2
b	·5780	1·3525	·0158	·0156	+2
c	·5461	1·3538	·0181	·0182	ref.
d	·4264	1·3613	·0289	·0289	ref.
e	·4082	1·3631	·0322^5	·0322	0·^{5}
f	·3922	1·3648	·0356	·0356	0
g	·3780	1·3666	·0390^5	·0390^5	0
h	·3651	1·3685	·0426^5	·0426^5	ref.
i	·3535	1·3704	·0467	·0467	0

It is clear from the form of the D graph that a two-constant formula cannot account for the rotary dispersion in this solution. Assuming $D = \frac{a_1}{1 - \lambda^{-2}\lambda_1^2} + a_2$, we find $\lambda_1 = \cdot 465\,\mu$. The low value for the principal absorption-band indicates the existence of another band in the ultra-violet. The wave-length of this absorption-band may be calculated approximately if we assume $\lambda_1 = \cdot 510\,\mu$.

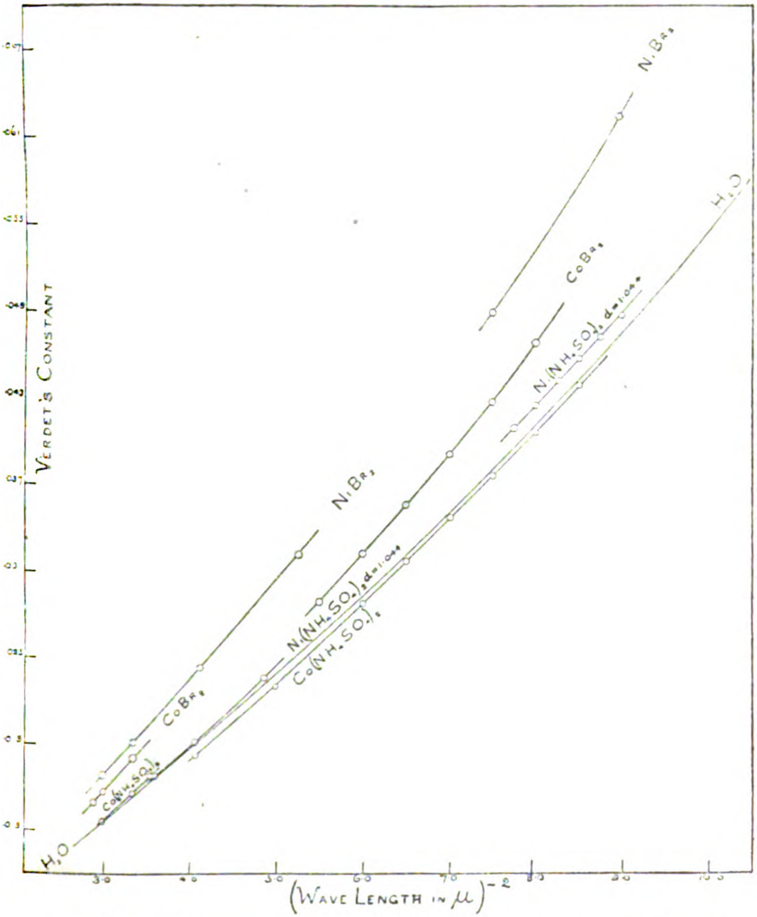
In this way we find

$$D = \frac{a_1}{1-\lambda^{-2}\lambda_1^{2}} + \frac{a_2}{1-\lambda^{-2}\lambda_2^{2}},$$

with

$$\lambda_1 = \cdot 510\ \mu, \qquad \lambda_2 = \cdot 246\ \mu,$$
$$a_1 = +9\cdot 7 \times 10^{-6}, \qquad a_2 = +5\cdot 65 \times 10^{-5}.$$

Fig. 2.



With this formula the values of R have been calculated. The position of the ultraviolet absorption-band seems satisfactory, judging from the absorption-curve given by Houstoun for a solution of $CoBr_2$. The value for λ_2 must be taken as an effective one only. Houstoun records an absorption-band at ·285 μ. According to Lübben *, the characteristic wave-length of the bromine anion is at ·186 μ in colourless solutions.

Cobalt Nitrate. (Fig. 3.)

$d=1·078$ gm. per c.c., $x=·980$.

Obs.	λ in μ.	n_{20}.	$R_{(obs.)}$.	$R_{(calc.)}$.	$\delta R\times 10^4$.
a	·5893	1·3572	·0128	·0128	ref.
b	·4200	1·3620	·0242	·0242	ref.
c	·4000	1·3639	·0278	·0277	+1
d	·3800	1·3663	·0317	·0317	ref.
e	·3600	1·3692	·0364	·0363	+1
f	·3500	1·3705	·0394	·0390	+4

With this solution, which was investigated before I had access to a mercury lamp, the rotation for only one line on the low-frequency side of the absorption-band could be determined. It is obvious from the difference graph that a two-constant formula cannot represent the dispersion. Introducing an extra constant, we find from

$$(abd),\quad \lambda_1=·471\,\mu,$$
$$(ace),\quad \lambda_1=·468\,\mu,$$
$$(bce),\quad \lambda_1=·411\,\mu,$$

with

$$D=\frac{a_1}{1-\lambda^{-2}\lambda_1{}^2}+a_2.$$

This progression is undoubtedly due to the presence of another free period in the ultraviolet. The formula does not give a value for this free period, probably owing to the comparatively large negative value of the constant a_2. Using the first of the above values for λ_1, we find

$$a_1 = +1·36^5\times 10^{-5},$$
$$a_1 = -6·64\times 10^{-5}.$$

Even with this small value of λ_1, the agreement between the calculated and observed values of R is satisfactory.

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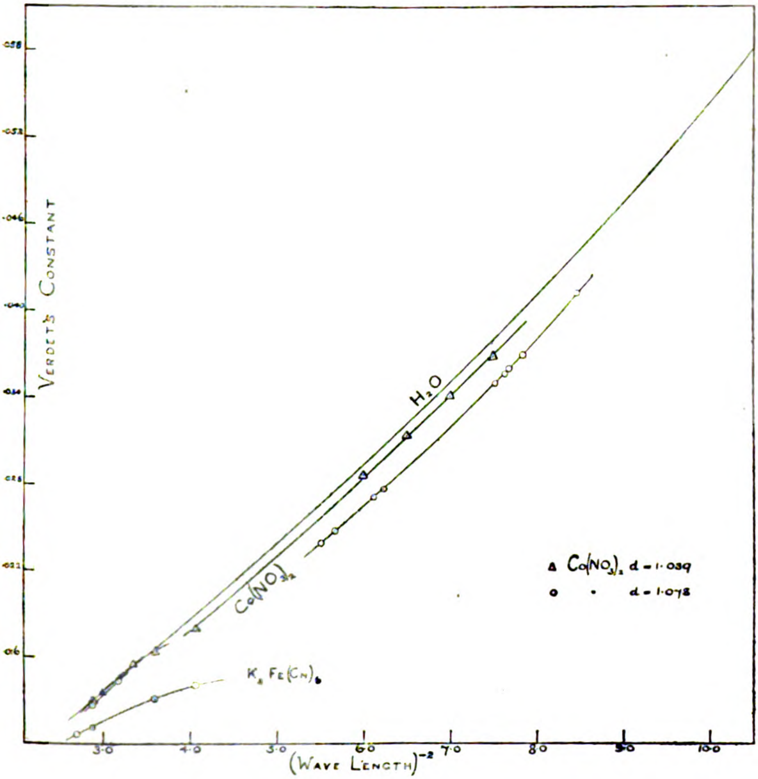
* *Ann. d. Phys.* xliv. p. 977 (1914).

The magnetic rotation in cobalt nitrate is interesting, as we find a negative value for D on the low-frequency side of the absorption-band. Ingersoll*, who has investigated the magnetic rotary dispersion of a number of nickel and cobalt salts in the near infra-red, finds this negative difference to persist as far into the infra-red as he was able to extend his observations. Wachsmuth † also gives the rotation of an aqueous solution of $Co(NO_3)_2$ to be less than that of water, the two rotations referring to the yellow sodium line. I intend to make a more complete investigation of solutions of $Co(NO_3)_2$ shortly.

Fig. 3.



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* Journ. Opt. Soc. Amer. vi. (Sept. 1922).

† *Wied. Ann.* xliv. p. 377 (1891).

Cobalt Ammonium Sulphate. (Fig. 2.)

$d=1{\cdot}050$ gm. per c.c., $x=\cdot 983$.

Obs.	λ.	n_{20}.	$R_{(obs.)}$.	$R_{(calc.)}$.	$\delta R\times 10^4$.
a	·5780	1·3439	·0136	·0143	−7
b	·5461	1·3450	$\cdot 0156^5$	·0166	$-9^{\cdot 5}$
c	·5270	1·3458	·0169	absorpt.	
d	·4958	1·3472	·0184	absorpt.	
e	·4472	1·3502	·0230	·0230	0
f	·4082	1·3534	·0288	·0288	0
g	·3922	1·3550	·0317	·0317	0
h	·3780	1·3566	·0347	·0346	+1
i	·3651	1·3582	·0376	·0377	−1
j	·3535	1·3597	·0406	·0408	−2
k	·3430	1·3614	·0439	·0439	0

If we try a three-constant formula for D we find from

$$(aef),\quad \lambda_1=\cdot 467\,\mu,$$
$$(ehk),\quad \lambda_1=\cdot 460\,\mu,$$
$$(beh),\quad \lambda_1=\cdot 480\,\mu.$$

Attributing this low value of λ_1 to the existence of another ultraviolet free period, and proceeding to calculate the corresponding wave-length λ_2, we find $\lambda_2=\cdot 510=\lambda_1$. This means that for this solution a two-constant formula

$$D\equiv\frac{a_1}{1-\lambda^{-2}\lambda_1^{\,2}}$$

is sufficient to account for the rotary dispersion.

Assuming $\lambda_1=\cdot 510\,\mu$, I find

$$a_1 = +9{\cdot}4\times 10^{-6}.$$

It thus appears that the rotary dispersion in $Co(NH_4SO_4)_2$ is conditioned almost entirely by a single free period corresponding to $\lambda_1=\cdot 510\,\mu$, the dispersive effect due to the ammonium sulphate radicle being almost nil. This statement seems to receive support from the behaviour of the refractive-index graph of this solution.

Nickel Solutions.

Nickel Bromide. (Fig. 2.)

$d = 1\cdot110$ gm. per c.c., $x = \cdot977$.

Obs.	λ in μ.	n_{20}.	$R_{(obs.)}$.	$R_{(calc.)}$.	$\delta R \times 10^4$.
a	·5780	1·3550	·0169	·0169	0
b	·5461	1·3569	·0192	ref.	—
c	·4916	1·3599	·0241	·0243	−2
d	·4358	1·3641	·0322	ref.	—
e	·3652	1·3721	$\cdot0488^5$	ref.	—
f	·3342	1·3776	·0623	·0618	+5

The rotations for the first three lines have been determined visually, and for the last three photographically. Owing to the small region of transmission in the ultraviolet, the rotation for the two ultraviolet lines $\cdot3652\,\mu$ and $\cdot3342\,\mu$ cannot be determined with as great an accuracy as is possible with the cobalt solutions. To reduce the time of exposure within reasonable limits the angle of half-shade must be increased, thereby losing sharpness of contrast between the parts of the divided field.

From the D curve, is seen the existence of slight anomalous dispersion at the band $\lambda = \cdot405\,\mu$. If we include a term to represent this band, we find

$$\lambda_1 = \cdot405\,\mu, \qquad \lambda_2 = \cdot215\,\mu,$$
$$a_1 = +1\cdot44 \times 10^{-6}, \quad a_2 = +1\cdot732 \times 10^{-4}.$$

It will be seen that the formula $D = \dfrac{a_1}{1 - \lambda^{-2}\lambda_1^2} + \dfrac{a_2}{1 + \lambda^{-2}\lambda_2^2}$ gives values of R which are quite close to the observed values.

Nickel Chlorate. (Fig. 1.)

$d = 1\cdot229$ gm. per c.c., $x = \cdot925$.

Obs.	λ in μ.	n_{20}.	$R_{(obs.)}$.	$R_{(calc.)}$.	$\delta R \times 10^4$.
a	·5780	1·3713	·0159	·0154	+5
b	·5461	1·3723	·0179	·0179	ref.
c	·4916	1·3750	·0226	·0226	0
d	·4358	1·3789	·0301	·0301	ref.
e	·3342	1·3919	·0569	·0569	ref.
f	·3128	1·3967	·0674	·0683	−9

As with the nickel-bromide solution, a three-constant formula for D does not give a possible value for λ_1. Assuming $\lambda_1 = \cdot 405\,\mu$, we find $\lambda_2 = \cdot 216\,\mu$,

giving $a_1 = 2\cdot 8 \times 10^{-6}$, $a_2 = 1\cdot 276 \times 10^{-4}$.

A less concentrated solution also showed anomalous dispersion at the principal absorption-band (see figs. 1 & 5).

Nickel Ammonium Sulphate. (Fig. 2.)

The differences for this solution were too small to admit of computation. The observed Verdet's constants are given in graphical form.

For the sake of convenience, the values of a_1 and a_2 have been collected along with the ratios $\frac{a_1}{c}$ and $\frac{a_2}{c}$, where c is the concentration of the salt in gm. per c.c. of solution.

	c.	$a_1 \times 10^4$.	$a_2 \times 10^4$.	$\frac{a_1}{c} \times 10^4$.	$\frac{a_2}{c} \times 10^4$.
$Co(ClO_3)_2$ (i.) ...	·480	+·407	− ·793	+ ·85	$-\cdot 16^{5}$
(ii.) ...	·092	+·067	− ·136	+ ·73	− ·15
$CoBr_2$	·110	+·097	+ ·565	+ ·88	+5·14
$Co(NO_3)_2$	·098	+·136	− ·664	+1·39	−6·78
$NiBr_2$	·133	+·014	+1·732	+ ·11	+13·02
$Ni(ClO_3)_2$	·304	+·028	+1·276	+ ·10	+ 4·20

It will be seen that, for the cobalt salts, the ratio $\frac{a_1}{c}$ is of the same order of magnitude and about 8 times greater than the ratio for the nickel salts. Owing to this comparatively small ratio for the nickel salts, the dispersion in the nickel solutions is controlled almost entirely by the ultraviolet free periods. The ratio $\frac{a_2}{c}$ varies in sign as well as magnitude. This is to be expected from the different meanings which have been attributed to a_2 in the different salts.

Miscellaneous Solutions.

The striking difference between the magnetic properties of potassium ferrocyanide and potassium ferricyanide encouraged the author to carry out some observations on the magnetic rotary dispersion of solutions of these salts in water. About a year after I had completed the observations on these solutions, I found from the references in Ingersoll's paper that Siertsema* had studied the magnetic rotary dispersion in an aqueous solution of potassium ferricyanide. The following table gives the author's results.

Potassium Ferricyanide. (Fig. 3.)

$d=1{\cdot}008$ gm. per c.c., $x=\cdot991$.

Obs.	λ in μ.	n_{20}.	$R_{(obs.)}$.	$R_{(calc.)}$.	$\delta R\times10^4$.
a	·6104	1·3353	·0107	·0105	+2
b	·5893	1·3360	·0112	·0112	ref.
c	·5270	1·3382	·0132	·0133	−1
d	·4958	1·3393	·0141	·0141	ref.

The line ·6104 μ was obtained by feeding the iron arc with lithium chloride. The observations on this line could not be made easily. No observations could be made on the apparently strong lithium line ·6708 μ.

The rotary dispersion curve obtained from a large number of observations on the lines tabulated above was so striking that it was suspected that changes had occurred in the solution while the observations were in progress. To ascertain if this was or was not the cause of the variation, another solution of almost the same concentration was prepared, and the observations taken in the reverse order. It was found that the curve given by this second solution was parallel to and above (corresponding to the smaller concentration of this solution) the original curve. The difference between the two curves is too small to be shown easily on fig. 3.

Taking the rotations for the lines ·5893 μ and ·4958 μ to be the more reliable, we find that with $D=\dfrac{a_1}{1-\lambda^{-2}\lambda_1^{2}}$, $\lambda_1=\cdot427\,\mu$, which does not seem an unreasonable value for the position of the absorption-band.

This value for λ_1 gives

$$a_1=-6{\cdot}04\times10^{-5}.$$

The rotations calculated for the lines ·6104 μ and ·5270 μ are not far from the observed values. A three-constant formula for D does not give a likely value for λ_1.

According to these results it is seen that the rotary dispersion in potassium ferricyanide is in accordance with Drude's molecular-current theory. As with $Co(ClO_3)_2$ and

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* *Arch. Néer.* (2) v. p. 447 (1900).

$Co(NO_3)_2$, the negative rotation of $K_3Fe(CN)_6$ arises from the electrons which contribute to the paramagnetism of the solution.

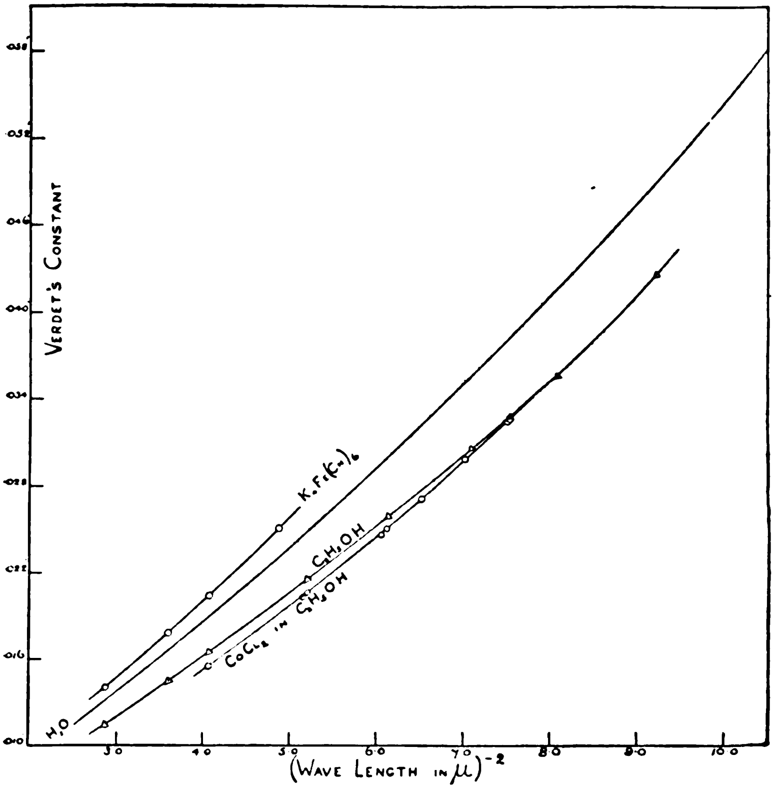
Siertsema states that the rotary dispersion in $K_3Fe(CN)_6$ is greater than the inverse fourth power of the wave-length. The above formula for D also gives the same result.

Potassium Ferrocyanide. (Fig. 4.)

$d=1{\cdot}076^5$ gm. per c.c., $x={\cdot}957$.

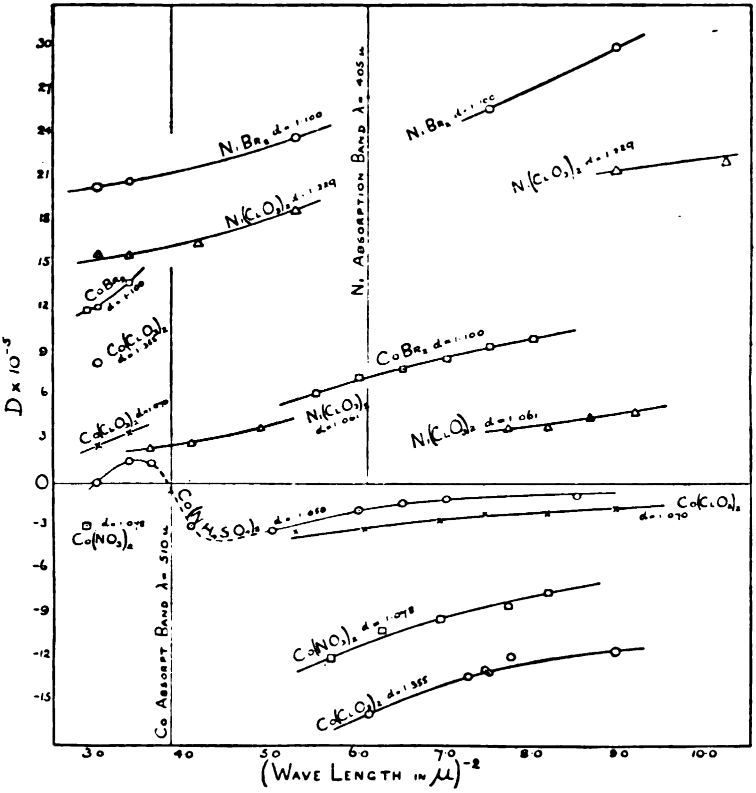
Obs.	λ.	n_{20}.	R.	$R_{calc.(5)}$.	$R_{calc.(10)}$.
a	·5893	1·3559	·0140	·0140	·0140
b	·5270	1·3585	·0178	·0178	·0178
c	·4958	1·3602	·0205	·0205	·0205
d	·4529	1·3631	·0251	·0251	·0251
e	·4406	1·3641	·0266	·0267	·0267

Fig. 4.



The rotary-dispersion curve of this solution follows the usual trend of such curves for diamagnetic substances. The rotations for the last two lines were obtained photographically. For this solution we can apply either equation (5) or equation (10) to calculate the rotary dispersion.

Fig. 5.



From equation (5) we obtain

$$a_1 = +3{\cdot}51 \times 10^{-5}, \quad \lambda_1 = {\cdot}170\,\mu.$$

Equation (10) gives

$$a_1 = +5{\cdot}98 \times 10^{-5}, \quad \lambda_1 = {\cdot}237\,\mu,$$

where, in both cases, a two-constant formula has been used for the differences Δ and D. The agreement between the values of the rotations calculated from (5) and (10) and the observed values is quite satisfactory. The decision as to

Fig. 6.

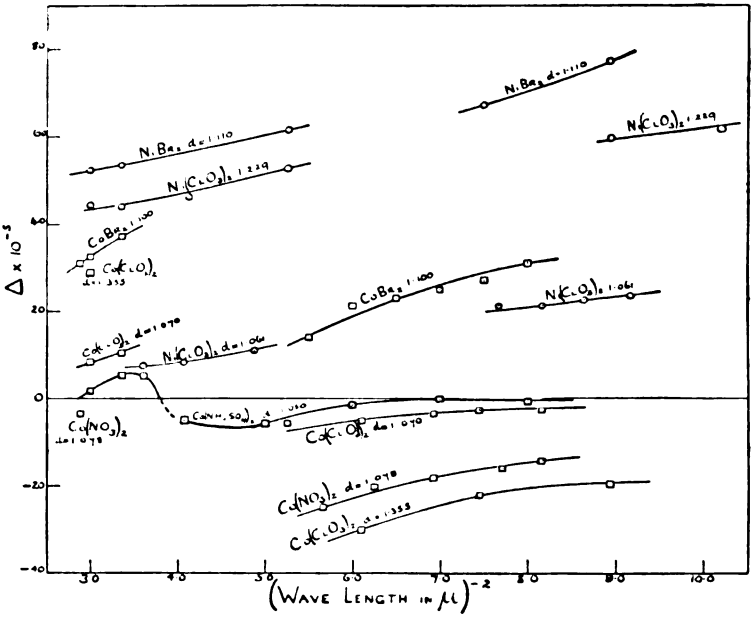
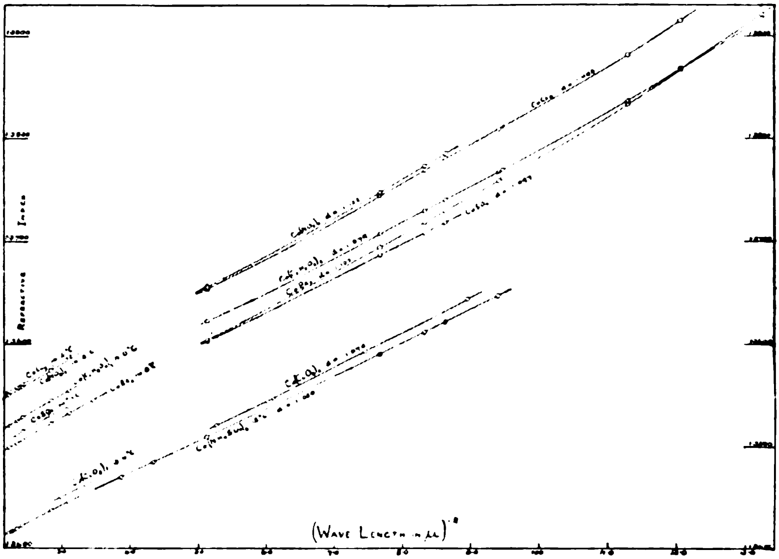

80
60
40
20
0
-20
-40
Δ × 10⁻⁵
N. Ba₂ d=1·110
N(C₂O₃)₂ 1·229
CoBa₂ 1·100
Co(C₂O₃)₂
d=1·355
Co(C₂O₃)₂ d=1·070
N(C₂O₃)₂ d=1·061
Co(NO₃)₂
d=1·070
Co(NH₄SO₄)₂ d=1·010
CoBa₂ 1·100
N(C₂O₃)₂ 1·061
N. Ba₂ d=1·110
N(C₂O₃)₂ 1·229
Co(C₂O₃)₂ d=1·070
Co(NO₃)₂ d=1·070
Co(C₂O₃)₂ d=1·355
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10·0
(Wave Length in μ)⁻²

Fig. 7.

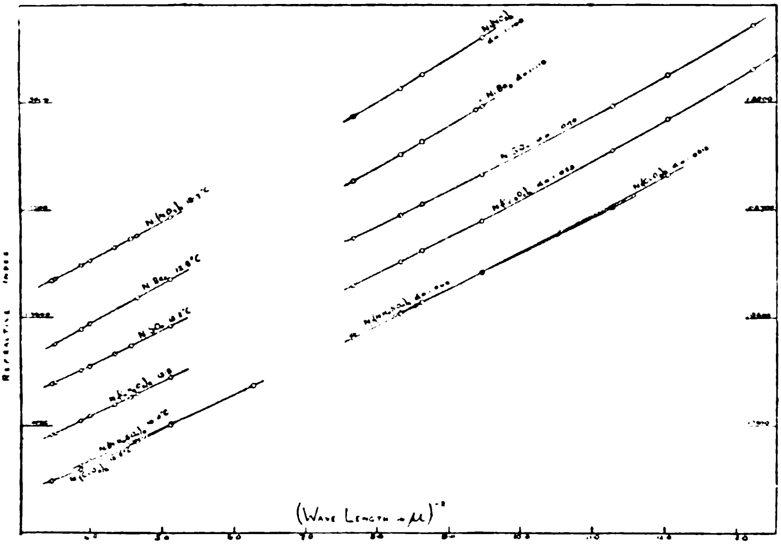

Refractive Index
(Wave Length in μ)⁻²

which formula is more valid must be left to refractive-index measurements in order to obtain the position of the absorption-bands.

Cobalt Chloride in Alcohol.

A dark-blue solution of cobalt chloride in ethyl alcohol gave a slight negative rotation, which decreased with decreasing wave-length. In accordance with Kundt's law, the cobalt absorption-band shifts towards the red end of the spectrum when the solvent changes from water to ethyl alcohol. This change makes it possible to carry out visual observations on the high-frequency side of the absorption-band, which cannot be made in an aqueous solution of $CoCl_2$. With the present arrangement of my apparatus it was impossible to make any observations on the low-frequency side of the absorption-band.

Fig. 8.



It will be seen that the rotary dispersion curve for the alcoholic solution shows the same general characteristics as the aqueous solution of $CoCl_2$ investigated in the previous communication.

SUMMARY.

1. The aqueous solutions of cobalt and nickel salts investigated show anomalous rotary dispersion at their principal absorption-bands. This anomalous rotary dispersion is much stronger for the cobalt solutions than for the nickel solutions.

2. The high-frequency electrons in cobalt solutions, as well as in $K_3Fe(CN)_6$, give rise to the negative rotation displayed by these salts.

3. The rotary dispersion in the solutions investigated may be calculated from the formula

$$\frac{\delta\lambda^2}{n(n^2+2)}=x\frac{\delta_\kappa\lambda^2}{n_\kappa(n_\kappa^2+2)}+\Sigma\frac{a_s}{1-\lambda^{-2}\lambda_s^2},$$

which is derived from Drude's molecular current hypothesis by taking into account the electric polarization of the liquids.

I desire to express my best thanks to Prof. Wilberforce for the interest he has taken in the experiments and for the facilities and apparatus placed at my disposal; to Dr. S. S. Richardson for the interest he has taken in the work and his helpful criticism of the paper; to Mr. W. L. Marshall, B.Sc., and Mr. J. Smith, M.Sc., for assistance in the graphical and electrolytic work.

The George Holt Physics Laboratory,
University of Liverpool.

XLII. *On the Principle of Huygens.* *By* W. ANDERSON, *B.Sc., Lecturer in Physics, The College of Technology, Manchester* *.

AN expression for the light disturbance s_0 at a point O, in terms of the values of s over a closed surface S surrounding O, has been given by Kirchhoff †, viz.

$$4\pi s_0=\int\left(\frac{\partial}{\partial r}\frac{s\left(t-\frac{r}{v}\right)}{r}\cos(nr)-\frac{1}{r}\frac{\partial}{\partial n}s\left(t-\frac{r}{v}\right)\right)dS, \quad (1)$$

where r is the distance of dS from O, n is the normal to dS drawn inwards, and $s\left(t-\frac{r}{v}\right)$ is what s becomes when $t-\frac{r}{v}$ is substituted in it for t.

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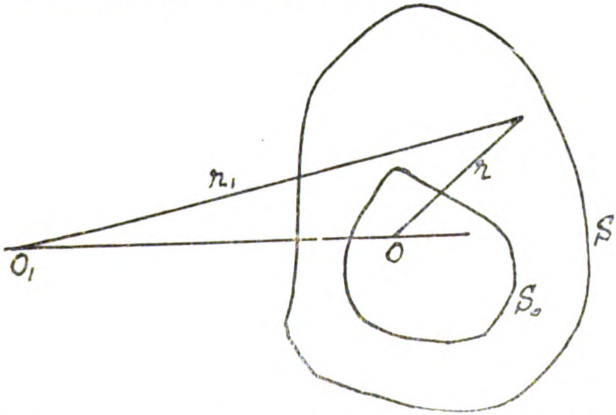
* Communicated by the Author.

† Wied. *Ann.* xviii. (1883).

It has been remarked by Larmor[*] that the usual modes[†] of deriving this general formula are "not free from analytical complexity." Since in the consideration of a number of diffraction problems it is sufficient to take the primary light wave as being completely given by $s=\frac{1}{r}f\left(t-\frac{r}{v}\right)$, the following derivation of (1) for this particular case may be of interest.

Let O_1 be a point source emitting a disturbance given by $s=\frac{1}{r_1}f\left(t-\frac{r_1}{v}\right)$ at points distant r_1 from O_1. If O is a point distant a from O_1, and S is a closed surface enclosing O, O_1 being outside S, the disturbance at O will be $s_0=\frac{1}{a}f\left(t-\frac{a}{v}\right)$ and we wish to express s_0 as an integral over S.



If F is a function of r_1 and r, the distances of any point from O_1 and O, and if $\frac{dF}{dr_1}$ denotes the whole rate of variation of F with r_1 along r_1, we have

$$\frac{dF}{dr_1}=\frac{\partial F}{\partial r_1}+\frac{\partial F}{\partial r}\cdot\frac{dr}{dr_1}. \quad . \quad . \quad . \quad . \quad (2)$$

If G is another function of r_1 and r, and $\frac{dG}{dr}$ is the whole rate of variation of G with r along r, we also have

$$\frac{dG}{dr}=\frac{\partial G}{\partial r}+\frac{\partial G}{\partial r_1}\cdot\frac{dr_1}{dr}. \quad . \quad . \quad . \quad . \quad (3)$$

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[*] Proc. L. M. S. ser. 2, i. p. 2 (1904).

[†] Drude, 'Theory of Optics,' Eng. ed. p. 169 (1902). Preston, 'Theory of Light,' 4th ed. p. 75 (1912).

Then it is easily seen geometrically that

$$\frac{dr}{dr_1} = \cos(r_1 r) = \frac{dr_1}{dr}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

where $\frac{dr}{dr_1}$ and $\frac{dr_1}{dr}$ have the same meanings as in (2) and (3).

Now if dv denotes an element of volume, and $d\omega$ an elementary solid angle with vertex at O_1, the value of $\int \frac{1}{r_1^2} \frac{dF}{dr_1} dv$ taken through the whole space enclosed by S will be

$$\int \frac{1}{r_1^2} \frac{dF}{dr_1} dv = \iint \frac{1}{r_1^2} \frac{dF}{dr_1} r_1^2 \, d\omega \, dr_1$$

$$= \int d\omega \int \frac{dF}{dr_1} \, . \, dr_1$$

$$= \int \frac{dS \cos(nr_1)}{r_1^2} \, . \, F,$$

the normal n to dS being drawn outwards. If S_0 is another surface enclosing O, and entirely inside S, the value of the above integral taken through the space between S_0 and S will be

$$\int \frac{1}{r_1^2} \frac{dF}{dr_1} dv = \int \frac{F \cos(nr_1)}{r_1^2} dS - \int \frac{F \cos(nr_1)}{r_1^2} dS_0 . \quad . \qquad (5)$$

In the same way we get

$$\int \frac{1}{r^2} \frac{dG}{dr} dv = \int \frac{G \cos(nr)}{r^2} dS - \int \frac{G \cos(nr)}{r^2} dS_0 , \quad . \qquad (6)$$

the volume integral being taken through the same region as before.

Combining (5) and (6) we get

$$\int \left(\frac{F \cos(nr_1)}{r_1^2} - \frac{G \cos(nr)}{r^2} \right) dS_0$$

$$= \int \left(\frac{F \cos(nr_1)}{r_1^2} - \frac{G \cos(nr)}{r^2} \right) dS$$

$$- \int \left(\frac{1}{r_1^2} \frac{dF}{dr_1} - \frac{1}{r^2} \frac{dG}{dr} \right) dv . \quad . \quad . \qquad (7)$$

If for S_0 we choose a spherical surface of indefinitely small radius and centre at O, and if G_0 is the value of G at O, this equation becomes

$$-4\pi G_0 = \int\left(\frac{F\cos(nr_1)}{r_1^2} - \frac{G\cos(nr)}{r^2}\right)dS, \quad . \quad (8)$$

provided that F and G are such that

$$\frac{1}{r_1^2}\frac{dF}{dr_1} - \frac{1}{r^2}\frac{dG}{dr} = 0\,;$$

that is, in virtue of (4),

$$\frac{1}{r_1^2}\frac{\partial F}{\partial r_1} - \frac{1}{r^2}\frac{\partial G}{\partial r} + \cos(r_1 r)\left(\frac{1}{r_1^2}\frac{\partial F}{\partial r} - \frac{1}{r^2}\frac{\partial G}{\partial r_1}\right) = 0.$$

Let us put

$$\frac{1}{r_1^2}\frac{\partial F}{\partial r_1} - \frac{1}{r^2}\frac{\partial G}{\partial r} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and

$$\frac{1}{r_1^2}\frac{\partial F}{\partial r} - \frac{1}{r^2}\frac{\partial G}{\partial r_1} = 0. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Then from (10) we shall have

$$\frac{F}{r_1^2} = \frac{\partial\phi}{\partial r_1}, \quad \frac{G}{r^2} = \frac{\partial\phi}{\partial r}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and using these values in (9) we get

$$\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial\phi}{\partial r_1}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right),$$

which may be written as

$$\frac{\partial^2}{\partial r_1^2}(r_1 r\phi) = \frac{\partial^2}{\partial r^2}(r_1 r\phi),$$

having for solution

$$r_1 r\phi = f(r_1 + r) + g(r_1 - r),$$

where f and g are any functions of $r_1 + r$, and $r_1 - r$.

If, therefore, we take $\phi = \frac{1}{r_1 r}f\left(t - \frac{r_1 + r}{v}\right)$, we get from (11) and (8)

$$-4\pi\left[r^2\frac{\partial}{\partial r}\frac{1}{r_1 r}f\left(t - \frac{r_1 + r}{v}\right)\right]_{r=0}$$

$$= \int\left[\frac{\partial}{\partial r_1}\frac{1}{r_1 r}f\left(t - \frac{r_1 + r}{v}\right)\cos(nr_1)\right.$$

$$\left. - \frac{\partial}{\partial r}\frac{1}{r_1 r}f\left(t - \frac{r_1 + r}{v}\right)\cos(nr)\right]dS.$$

The left-hand side of this equation is

$$-4\pi\left[-\frac{1}{r_1}f\left(t-\frac{r_1+r}{v}\right)-\frac{r}{r_1}f'\left(t-\frac{r_1+r}{v}\right)\right]_{r=0}$$

$$=4\pi\frac{1}{a}f\left(t-\frac{a}{v}\right)$$

$$=4\pi s_0.$$

Hence if we draw the normal inwards we have

$$4\pi s_0=\int\Bigg[\frac{\partial}{\partial r}\frac{\frac{1}{r_1}f\left(t-\frac{r_1+r}{v}\right)}{r}\cos(nr)$$

$$-\frac{1}{r}\frac{\partial}{\partial r_1}\frac{1}{r_1}f\left(t-\frac{r_1+r}{v}\right)\cos(nr_1)\Big)\Bigg]dS$$

as our required expression, or

$$4\pi s_0=\int\Bigg[\frac{\partial}{\partial r}\frac{s\left(t-\frac{r}{v}\right)}{r}\cos(nr)$$

$$-\frac{1}{r}\frac{\partial}{\partial r_1}s\left(t-\frac{r}{v}\right)\cos(nr_1)\Bigg]dS \quad . \quad . \quad . \quad . \tag{12}$$

If the normal is (l, m, n) and the origin is at O,

$$r_1^2=(x+a)^2+y^2+z^2,$$

and $$\frac{\partial s}{\partial r_1}\cos(nr_1)=\frac{\partial s}{\partial r_1}\left(l\frac{x+a}{r_1}+m\frac{y}{r_1}+n\frac{z}{r_1}\right)$$

$$=l\frac{\partial s}{\partial r_1}\frac{\partial r_1}{\partial x}+m\frac{\partial s}{\partial r_1}\frac{\partial r_1}{\partial y}+n\frac{\partial s}{\partial r_1}\frac{\partial r_1}{\partial z}$$

$$=l\frac{\partial s}{\partial x}+m\frac{\partial s}{\partial y}+n\frac{\partial s}{\partial z}$$

$$=\frac{\partial s}{\partial n},$$

and using this in (12) we get (1).

XLIII. *Theory of the Width of the Modified Spectrum Lines in the Compton Effect.* By G. E. M. JAUNCEY, *D.Sc., Associate Professor of Physics, Washington University, St. Louis, U.S.A.*[*]

1. *Introduction.*

A. H. COMPTON[†] has proposed a theory of the scattering of X-rays based upon the postulate that each quantum of X-rays is scattered by an individual electron. This theory requires that the wave-length λ_ϕ of the X-rays scattered in a direction ϕ with the direction of the primary X-rays should differ from the wave-length λ_0 of the primary rays by an amount

$$\lambda\phi-\lambda_0=h(1-\cos\phi)/mc, \quad . \quad . \quad . \quad . \quad (1)$$

where h is Planck's constant, m is the rest mass of the electron, and c is the velocity of light. If the change of wave-length is expressed in Å.U., equation (1) may be written

$$\lambda_\phi-\lambda_0=0\cdot0242(1-\cos\phi). \quad . \quad . \quad . \quad (2)$$

Compton has tested this formula experimentally[‡], and has found very good agreement with the theory when Mo Kα X-rays are scattered by graphite. Compton's results for the scattering of Mo Kα X-rays have been verified by others. However, all observers find that part of the X-rays are scattered with, and part without, change of wave-length. Compton calls the former modified scattered rays, and the latter unmodified rays. The unmodified rays give a spectrum line whose width is equal to that of the spectrum line of the primary rays. On the other hand, Compton's curves[‡] show an increased width in the modified spectrum line. For instance, his curves for scattering at 90° show the modified spectrum line as having an extreme angular width of about 15 minutes of arc greater than the width of the unmodified line. This signifies a wave-length width of 0·027 Å.U. since a calcite crystal was used. Now the primary rays which are incident on the effective part of the scattering substance have an angular width of probably not more than 20°. This would account for a wave-length width of 0·008 Å.U. due to the variation of ϕ in equation (2). There remains therefore a wave-length width of between 0·019 Å.U. and 0·027 Å.U. which is not due to the variation of ϕ. In this paper it is sought to explain this width.

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[*] Communicated by the Author.

[†] A. H. Compton, Phys. Rev. xxi. p. 483 (1923).

[‡] A. H. Compton, Phys. Rev. xxii. p. 408 (1923).

2. *Theory.*

The quantum theory of Compton * is extended to the case where the binding energy of the electron has to be taken into account. The energy relation is then

$$hc/\lambda_0 = hc/\lambda_\phi + hc/\lambda_s + mc^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right) + MV^2/2, \quad (3)$$

where λ_s is a critical absorption wave-length of the scattering substance, and where the third and fourth terms on the right-hand side represent the kinetic energy of the recoiling electron and that of the rest of the atom from which the recoil electron is separated respectively. This last term, however, is negligible, due to the mass of the rest of the atom being great compared with that of the recoil electron.

Next we consider the momentum relation. Referring to fig. 1, OA represents the magnitude and direction of the momentum of the primary quantum h/λ_0, OB the momentum of the scattered quantum h/λ_ϕ, BC the momentum of the recoil electron $m\beta c/\sqrt{1-\beta^2}$, and CA the momentum of the rest of the atom from which the recoil electron is separated by the scattering process. We then have the vector equation

$$OA = OB + BC + CA, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where OA is along the x-axis and OB in the xy plane, but BC and CA are not necessarily in the xy plane. We next make the restriction that the momentum CA of the rest of the atom is equal but opposite in direction to the momentum of the electron in its Bohr orbit just before scattering takes place. The justification for this restriction is that the rest of the atom and the electron are each revolving about their common centre of mass before scattering takes place. If we assume that the action between the quantum and the electron takes place in a time very small compared with the period of the electron in its orbit, then the electron can be thought of as being suddenly removed from its orbit, and the centre of mass of the rest of the atom will continue in motion along the tangent to its orbit about the common centre of mass which existed just before the removal of the electron from the atom. Since the velocity due to thermal agitation is small, we may neglect the momentum of the atom as a whole before the removal of the electron. This requires that the momentum of the rest of the atom be equal and opposite to that of the electron before removal of the latter. We have therefore that AC (= − CA, fig. 1) represents the momentum of the electron in its Bohr orbit.

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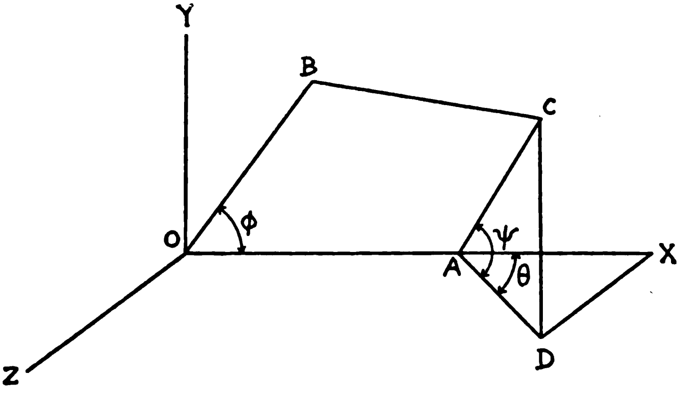
* A. H. Compton, Phys. Rev. xxi. p. 483 (1923).

We shall now find an expression for the momentum of an electron in its Bohr orbit in terms of the binding energy of the electron in that orbit. For simplicity let us assume that the orbit is circular. Using the relativity mass of the electron at high speeds, we have the centrifugal force relation

$$\frac{m\beta_s^2c^2}{r\sqrt{1-\beta_s^2}} = \frac{Ee}{r^2}, \quad \ldots\ldots \quad (5)$$

where r is the radius of the circular orbit, E is the effective nuclear charge, and $\beta_s c$ is the velocity of the electron in its orbit. The binding energy of the electron in its orbit is equal to minus the total energy of the electron in its orbit, and therefore

Fig. 1.



$$hc/\lambda_s = Ee/r + mc^2(1-1/\sqrt{1-\beta_s^2}). \quad \ldots \quad (6)$$

From equations (5) and (6) we obtain

$$\beta^2 = 2\alpha_s - \alpha_s^2, \quad \ldots\ldots \quad (7)$$

where $\alpha_s = h/mc\lambda_s$. The momentum of the electron in its orbit is therefore $mc\alpha_n$, where

$$\alpha_n = \beta_s/\sqrt{1-\beta_s^2} = \sqrt{2\alpha_s-\alpha_s^2}/(1-\alpha_s). \quad \ldots \quad (8)$$

The length of AC (fig. 1) represents $mc\alpha_n$, and is therefore constant. The locus of C is therefore a sphere with A as centre.

In fig. 1, AD is the projection of AC on the plane XOZ.

The angle CAD is represented by ψ, and the angle XAD by θ. Since BC represents $m\beta c/\sqrt{1-\beta^2}$, we have, dividing throughout by m^2c^2,

$$\begin{aligned}\beta^2/(1-\beta^2) = \alpha_0^2+\alpha_\phi^2+\alpha_n^2-2\alpha_0\alpha_\phi\cos\phi \\ -2\alpha_n\alpha_\phi\cos\psi\cos\theta\cos\phi \\ +2\alpha_0\alpha_n\cos\psi\cos\theta-2\alpha_\phi\alpha_n\sin\psi\sin\phi, \quad (9)\end{aligned}$$

where $\alpha_0 = h/mc\lambda_0$ and $\alpha_\phi = h/mc\lambda_\phi$. From equation (3) we have, neglecting the energy of the rest of the atom,

$$\beta^2/(1-\beta^2) = \alpha_0^2+\alpha_\phi^2+\alpha_s^2+2\alpha_0-2\alpha_s-2\alpha_0\alpha_\phi-2\alpha_0\alpha_s+2\alpha_\phi\alpha_s. \quad . \quad . \quad . \quad (10)$$

Equating the right-hand sides of equations (9) and (10), and solving for α_ϕ, we have

$$\alpha_\phi = \frac{\alpha_0(1-\alpha_s-\alpha_n\cos\psi\cos\theta)-\alpha_s-(\alpha_n^2-\alpha_s^2)/2}{1+\alpha_0(1-\cos\phi)-\alpha_s-\alpha_n(\cos\psi\cos\theta\cos\phi+\sin\psi\sin\phi)}. \quad . \quad . \quad . \quad (11)$$

Although equation (11) has been obtained on the assumption that the momentum of the rest of the atom is equal but opposite to that of the electron in its orbit, yet the equation is true even without this restriction provided that $mc\alpha_n$ is the momentum of the rest of the atom in the direction CA (fig. 1) after scattering has taken place. A. H. Compton* has recently described a general quantum theory of scattering in which he arrives at an equation which is similar to equation (11). He however does not make the restriction given by equation (8), although he takes account of the binding energy of the electron in its orbit.

Referring to equation (11), we see that α_ϕ varies with θ and ψ, the scattering angle ϕ being constant. This variation of α_ϕ causes a variation of λ_ϕ, the scattered wave-length due to the relation

$$\alpha_\phi = h/mc\lambda_\phi. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

From equations (11) and (12) we have

$$\lambda_\phi = \lambda_0 \cdot \frac{w-v(\cos\psi\cos\theta\cos\phi+\sin\psi\sin\phi)}{u-v\cos\psi\cos\theta}, \quad (13)$$

where

$$u = 1-\alpha_s-\alpha_s/\alpha_0-(\alpha_n^2-\alpha_s^2)/2\alpha_0,$$

$$v = \alpha_n,$$

and

$$w = 1+\alpha_0(1-\cos\phi)-\alpha_s.$$

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* A. H. Compton, Phys. Rev. xxiv. p. 168 (1924).

Let us move the origin of coordinates from O to A (fig. 1), and let the cartesian coordinates of C then be x, y, z, Since $AC = \alpha_n = v =$ constant, we have $\cos\psi\cos\theta = x/v$ and $\sin\psi = y/v$; so that from equation (13)

$$\lambda_\phi = \lambda_0 . \frac{w - x\cos\phi - y\sin\phi}{u - x} \quad . \quad . \quad . \quad . \quad (14)$$

Hence, for $\lambda_\phi =$ const., equation (14) shows that the locus of C is on the intersection of the plane represented by equation (14), and the sphere $x^2 + y^2 + z^2 = v^2$. Also, since there is no term in z in equation (14), the plane is parallel to the axis of z. The maximum and minimum values of λ_ϕ ($\phi =$ const.) are therefore given by the two planes, equation (14), which touch the sphere. Since the planes are parallel to the axis of z, the problem reduces to finding the two lines in the xy plane which touch the circle $x^2 + y^2 = v^2$. Now the condition that the line represented by equation (14) may touch the circle is that

$$(u^2 - v^2)l^2 - 2(uw - v^2\cos\phi)l + w^2 - u^2 = 0, \quad . \quad (15)$$

where $l = \lambda_\phi/\lambda_0$. Solving, we obtain

$$l = \frac{uw - v^2\cos\phi \pm v\sqrt{u^2 + w^2 - 2uw\cos\phi - v^2\sin^2\phi}}{u^2 - v^2} \quad . \quad (16)$$

The extreme variation of λ_ϕ is therefore

$$\delta\lambda_\phi = \frac{2v\lambda_0\sqrt{u^2 + w^2 - 2uw\cos\phi - v^2\sin^2\phi}}{u^2 - v^2} . \; . \quad (17)$$

This is the formula for the wave-length width of a modified spectrum line in the Compton effect. The change of wave-length for the centre of the line is given by

$$\lambda_\phi - \lambda_0 = \lambda_0\left(\frac{uw - v^2\cos\phi}{u^2 - v^2} - 1\right) . \quad . \quad . \quad . \quad (18)$$

Equation (17), although exact, is difficult to handle. It may, however, be put into an approximate form which is sufficiently correct so long as α is very much smaller than α_0. We then have from equation (8) that $\alpha_n = \sqrt{2\alpha_s}$, and approximately $u = 1$, $v = \sqrt{2\alpha_s}$, and $w = 1$. These approximations give

$$\delta\lambda_\phi = 4\lambda_0 \sin\frac{\phi}{2} \sqrt{2h/mc\lambda_s} . \quad . \quad . \quad . \quad . \quad (19)$$

3. *Comparison with Experiment, and Discussion.*

For the scattering of Mo $K\alpha$ X-rays by the L electrons of carbon we have $\lambda_0 = 0{\cdot}71$ Å.U. and $\lambda_s = 360$ Å.U.*, making $\alpha_0 = 0{\cdot}034$ and $\alpha_s = 0{\cdot}000067$. Inserting these values in equation (19), we have

$$\delta\lambda_\phi = 0{\cdot}031 \sin\frac{\phi}{2} \quad . \quad . \quad . \qquad (20)$$

For scattering at $\phi = 90°$, equation (20) gives $\delta\lambda_\phi = 0{\cdot}022$ Å.U., while Compton's value, previously quoted, is less than 0·027 Å.U. More recently Compton and Woo † have published experimental curves showing the change of wave-length of Mo $K\alpha$ X-rays when scattered by various light elements. For scattering by carbon at $\phi = 128°$, their curve shows $\delta\lambda_\phi < 0{\cdot}0264$ Å.U., while equation (20) gives $\delta\lambda_\phi = 0{\cdot}0278$ Å.U. Thus for scattering by carbon, the experimental values agree fairly well with the theoretical values. Now, for scattering by the L electrons of aluminium, λ_s is about 150 Å.U., so that $\alpha_s = 0{\cdot}000162$, and equation (19) becomes

$$\delta\lambda_\phi = 0{\cdot}051 \sin\frac{\phi}{2} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (21)$$

Hence, scattering of Mo $K\alpha$ X-rays by aluminium at $\phi = 125°$ should give $\delta\lambda_\phi = 0{\cdot}0454$ Å.U. Compton and Woo's curve for aluminium shows about the same width for aluminium as for carbon—that is, less than 0·027 Å.U. Hence it seems as though the theoretical formula predicts a width which is greater than the experimental value for aluminium.

Now equation (19) rests upon the restrictive assumption that the momentum of the rest of the atom is equal but opposite to that of the electron in its orbit just before scattering takes place, and this assumption rests upon the further assumption that the action between the quantum and the electron is sudden. However, "suddenness" is a relative term. The action probably has some duration of time. We can probably say that the action is sudden if its duration is small compared with the period of revolution of the electron in its Bohr orbit. As the atomic number increases, the period of revolution decreases. For a very slow action between the quantum and the electron the width would be very small, because in such a case the position of the electron in its orbit at the beginning of the action would have only a small effect on the change of wave-length. It would seem, therefore, that my formula, equation (19), only holds for small values of α_s; that is, for small binding energies. For larger binding energies the experimental width is less than that given by equation (19)*. A second reason for the smallness of the experimental width for aluminium is that in Compton and Woo's curve for aluminium the hump for the scattering by the L electrons includes also the scattering by the M electrons. The width of the line due to the M electrons is much smaller than that due to the L electrons. It should not be forgotten that we have only considered the electrons as revolving in circular orbits in our theory, whereas in a complete theory elliptic orbits should also be considered. The effect of elliptic orbits will be discussed in another article.

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* A. L. Hughes, Phil. Mag. xliii. p. 145 (1922).

† Compton and Woo, Proc. Nat. Acad. Sci. x. p. 271 (1924).

Just what would be the effect on the change of wave-length when the action between the quantum and the electron is slow depends upon what we assume to be the mechanical system of the inside of the atom, and very little is known is about intra-atomic mechanics. Compton †, in his paper on the general quantum theory of scattering, makes two alternative assumptions: (*a*) that $\alpha_n = \alpha_s$, $\theta = 0$, and $\psi = \pi$; and (*b*) that the momentum of the recoil electron is zero, although the electron is removed to the outside of the atom. Both of these assumptions require a slow action between the quantum and the electron. It appears to the writer that a careful study, both experimental and theoretical, of the width of the modified lines in the Compton effect for primary X-rays of various wave-lengths and for various scattering substances may throw some light on the time of the action between the quantum and the electron in the scattering process.

Washington University,
St Louis, Mo., U.S.A.,
July 24, 1924.

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* *Note added during proof reading.*—The restrictive assumption above mentioned is only valid if, in addition to the time of action being small, the time taken by the recoil electron in escaping from the electrostatic field of the rest of the atom after it has been removed from its Bohr orbit is small. Hence equations (17), (18), and (19) only hold for small values of the binding energy of the scattering electron. For values of the binding energy comparable with the energy of the primary quantum the wave-length width of the modified spectrum line is less than that given by equations (17) and (19).

† A. H. Compton, Phys. Rev. xxiv. p. 168 (1924).

XLIV. *A New Discussion of Bucherer's Experiment.*
By U. Doi*.

[Plate VI.]

1. *Introductory Note.*

The present writer in 1922† put forward a theory of relativity in which, however, Einsteinian relativity of space and time is excluded.

Following on a discussion with Einstein during his visit to Japan the writer has sought to obtain experimental evidence of his theory. Some investigations which support it will appear in the forthcoming 'Proceedings of the Physico-Mathematical Society of Japan.'

The following discussion of Bucherer's experiments, which is the main subject of the present paper, is taken up for the purpose of showing another example of experimental evidence therein in favour of the writer's theory, and against Einstein's one, contrary to what the author of the experiments, Bucherer, has concluded himself.

2. *Bucherer's Experiment.*

By a very ingenious experiment, published in 1909‡, on the deflexion of the β-particles emitted with large velocities from radium fluoride set in the crossed field of electric and magnetic forces, Bucherer confirmed decisively that the amount of deflexion of an electron tends to zero as its velocity approaches that of light c. But the acceleration of an electron moving with the velocity v perpendicular to a magnetic field of the intensity H is proportional to $\frac{e}{m}v\mathrm{H}$. From an action of this sort in essence originated the above said deflexion of the β-particles in Bucherer's experiment. Thus, Bucherer's experimental conclusion as expressed by an equation is

$$\lim_{\beta=1}\frac{e}{m}\beta=0,$$

in which β stands, as usual, for the ratio $\frac{v}{c}$. So far there may be no room for argument.

At the time when Bucherer experimentally confirmed the above relation there were prevailing two rival theories—one of Abraham and another of Lorentz—as to the constitution of an electron. So he made use of his experimental results, as his second step, to decide between these two rival theories. In this second step, Bucherer's conclusion from his data was that the preference was assuredly for the Lorentz theory, or, which comes to the same thing, for Einstein's theory of relativity.

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* Communicated by the Author.

† U. Doi, 'The Anti-Einstein Theory of Relativity,' 1922 (Japanese edition).

‡ *Ann. der Phys.* vol. xxviii. p. 513 (1909).

On examining closer, however, the photographic records of the experiments, the present writer has found that they do not, either, afford evidence in favour of Lorentz-Einstein's theory. As will be seen in the following, on the contrary, there is exposed in them a serious discrepancy with what is claimed by that theory, while with the writer's theory they are in good agreement, almost to a degree of coincidence.

Now, fixing our attention to a particle with an initial velocity v in a direction making an angle α with that of the magnetic field, the condition for it to escape from between the condenser plates is *

$$evH \sin \alpha = eX, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where X is the electric intensity between the plates.

After leaving the plates, the particle follows a spiral path, deviating thus out of the vertical plane in which its initial motion has been confined. But it will be shown later in §4, that the amount of deviation of the sort is so small that the general form of the curve of velocity-function of an electromagnetic mass remains unaffected if we neglect it. And the matter is simplified. We have the above relation (1) for every β-particle that escapes from between the condenser plates, all the way along a circular arc confined within a respective vertical plane up to the photographic film. But the radius r of the circular arc described by the particle satisfies the equation

$$m\frac{v^2}{r} = evH \sin \alpha. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Elimination of v between the above two equations (1) and (2) gives

$$r = \frac{X}{H^2} \cdot \frac{m}{e} \cdot \frac{1}{\sin^2 \alpha}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

On the other hand we have

$$(r-z)^2 = r^2 - a^2,$$

or

$$z = r - \sqrt{r^2 - a^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where z is the amount of the vertical deflexion of the

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* For details the reader is referred to Bucherer's original paper.

particles on the film from the undeflected trace, and a, the *effective* distance * between the end of the condenser plates and the film. Thus, combining the equations (3) and (4), we are able to find the theoretically expected value of z corresponding to any assigned value for α, provided the functional form of $\frac{m}{e}$ in terms of α is given.

Now, by Einstein's theory it is deduced to be, as is well known by the name of Lorentz's formula,

$$\frac{m}{e}=\frac{m_0}{\sqrt{1-\beta^2}}\cdot\frac{1}{e}=\frac{m_0}{e}\,\frac{1}{\sqrt{1-\beta^2}}.$$

But from the equation (1),

$$\beta=\frac{v}{c}=\frac{\mathrm{X}}{c\mathrm{H}}\,\frac{1}{\sin\alpha}.$$

Denoting $\frac{\mathrm{X}}{c\mathrm{H}}=[\beta]_{\alpha=\frac{\pi}{2}}$ by $\sin\alpha_0$ we have

$$\beta=\frac{\sin\alpha_0}{\sin\alpha}.$$

Thus,

$$\frac{m}{e}=\frac{m_0}{e}\,\frac{\sin\alpha}{\sqrt{\sin^2\alpha-\sin^2\alpha_0}}.$$

By the writer's theory, on the other hand, it is †

$$\frac{m}{e}=\frac{m_0}{(1-\beta^2)^2}\Big/\frac{e_0}{1-\beta^2}=\frac{m_0}{e_0}\,\frac{1}{1-\beta^2},$$

or

$$\frac{m}{e}=\frac{m_0}{e_0}\,\frac{\sin^2\alpha}{\sin^2\alpha-\sin^2\alpha_0}.$$

Hence, according to Einstein's theory,

$$\left.\begin{aligned}&z=r-\sqrt{r^2-a^2},\\&r=\mathrm{C_E}\,\frac{1}{\sin\alpha\,\sqrt{\sin^2\alpha-\sin^2\alpha_0}},\quad\left(\mathrm{C_E}=\frac{\mathrm{X}}{\mathrm{H}^2}\,\frac{m_0}{e}\right);\end{aligned}\right\}\quad.\qquad(5)$$

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[*] This *effective* distance is a little smaller than the actual geometrical one. Bucherer denotes it by $a-p$. See *Ann. der Phys.* loc. cit. p. 523.

[†] Author's 'Anti-Einstein Theory of Relativity,' *loc. cit.* p. 247.

while according to the other theory

$$\left.\begin{aligned} z&=r-\sqrt{r^2-a^2},\\ r&=C_D\frac{1}{\sin^2\alpha-\sin^2\alpha_0},\quad \left(C_D=\frac{X}{H^2}\frac{m_0}{e_0}\right). \end{aligned}\right\}\quad . \quad . \quad . \quad (6)$$

Comparing the calculated values for z with the actually obtained results on Bucherer's photographic films, we may be able to decide which of the two theories is to be preferred.

With Abraham's formula for $\frac{m}{e}$, z is not so simple a function in terms of α as in the above two equations. To avoid the complicated calculations for each separate photographic curve, therefore, Bucherer restricted himself to a comparison with one another of the maximum deflexions in a series of curves obtained with different conditions, which was sufficient, too, at the time for his purpose of distinguishing between Abraham's and Lorentz's formulæ.

In our present case, however, it is but an easy task to evaluate z corresponding to various values of α, two or three, at most, significant figures being sufficient for our purpose. Indeed, the sets of equations (5) and (6) may be transformed, in form, respectively into

$$\left.\begin{aligned} z&=r-\sqrt{r^2-a^2}=r-r\cos\left(\sin^{-1}\frac{a}{r}\right),\\ r&=C_E\frac{1}{\sin\alpha\sqrt{\sin^2\alpha-\sin^2\alpha_0}}=\frac{C_E}{\sin\alpha\{\sin(\alpha+\alpha_0)\sin(\alpha-\alpha_0)\}^{\frac{1}{2}}}; \end{aligned}\right\}$$

and . . . . (5)′

$$\left.\begin{aligned} z&=r-r\cos\left(\sin^{-1}\frac{a}{r}\right),\\ r&=C_D\frac{1}{\sin^2\alpha-\sin^2\alpha_0}=\frac{C_D}{\sin(\alpha+\alpha_0)\sin(\alpha-\alpha_0)}. \end{aligned}\right\}\quad (6)'$$

The results of calculation are given in Table I. and Table II., corresponding respectively to Bucherer's experiments No. 7 and No. 15.

The figures in the last columns of both tables are rough results of the writer's readings, by means of a microscopic comparator, of the photographic curves on the negative plates reproduced in equal dimensions from the prints, in the *Annalen der Physik*, of Bucherer's original films. It will be seen at once that they are in by far the better agreement with the writer's values than with those of Lorentz-Einstein.

TABLE I.
(For Experiment No. 7.)

a.	$\beta=\frac{v}{c}$.	x in mm.	z_E in mm.	z_D in mm.	$z_{\text{photogr.}}$ in mm.
25° 21′ ...	0·9999	99	0	0	—
26° 21′ ...	0·9645	97·47	0·69	0·20	—
27° 21′ ...	0·9318	95·94	1·04	0·41	0·5
28° 21′ ...	0·9015	94·41	1·30	0·62	0·7
29° 21′ ...	0·8734	92·88	1·57	0·83	0·8
30°.........	0·8562	91·90	1·72	0·98	1·0
34°.........	0·7656	85·76	2·70	1·91	1·9
38°.........	0·6954	79·63	3·66	2·90	2·9
42°.........	0·6398	73·50	4·66	3·95	3·9
46°.........	0·5951	67·38	5·66	5·02	4·9
50°.........	0·5589	61·25	6·68	6·11	6·0
55°.........	0·5226	53·60	7·95	7·47	7·5
60°.........	0·4943	45·94	9·18	8·79	8·8
65°.........	0·4725	38·28	10·34	10·04	10·0
70°.........	0·4556	30·63	11·38	11·18	11·2
75°.........	0·4432	22·97	12·27	12·14	12·1
80°.........	0·4347	15·31	12·89	12·88	12·8
85°.........	0·4297	7·66	13·36	13·35	13·3
90°.........	0·4281	0	13·50	13·50	13·5

$\log a=0{\cdot}59226$, $\log C_E=0{\cdot}75805$, $\log C_D=0{\cdot}71408$.

x measures the distance along the zero-line from the point of maximum deflexion, or the middle-point between the two vanishing ends of the curve.

3. *Comparison of Theoretical with Photographic Curves.*

It is not merely the matter of numerical values, however, that distinguishes the two theories from each other, but the essential character of the curve is different, as claimed by one or the other of the theories. There are two peculiar features, at least, worthy of our notice. First, the tangent of the angle of the limiting inclination of the curve at its vanishing ends to the undeflected line is infinite according to Einstein's equations (5), while it is finite according to the other (6). Next, according to (5), the curve is concave towards the undeflected line throughout the whole of its length; while, according to the other, it is convex at near its vanishing ends, and then becomes concave towards the undeflected line, thus giving a point of inflexion between the two regions of opposite concavity.

TABLE II.

(For Experiment No. 15.)

α.	$\beta=\frac{v}{c}$.	x in mm.	z_E in mm.	z_D in mm.	$z_{\text{photogr.}}$ in mm.
31°	1·0007	95	0	0	—
32°	0·9727	93·39	0·75	0·21	—
33°	0·9464	91·78	1·08	0·41	0·5
34°	0·9217	90·17	1·39	0·62	0·7
35°	0·8986	88·56	1·65	0·84	0·9
37°	0·8565	85·34	2·12	1·27	1·2
40°	0·8019	80·51	2·80	1·96	2·0
42°	0·7703	77·29	3·24	2·41	2·5
45°	0·7289	72·46	3·90	3·11	3·2
47°	0·7048	69·24	4·34	3·58	3·6
50°	0·6728	64·41	4·98	4·28	4·3
52°	0·6541	61·19	5·41	4·75	4·7
55°	0·6292	56·36	6·03	5·45	5·4
57°	0·6146	53·14	6·43	5·89	5·9
60°	0·5952	48·30	7·03	6·56	6·5
65°	0·5687	40·25	7·94	7·60	—
70°	0·5485	32·20	8·75	8·52	8·5
75°	0·5336	24·16	9·43	9·28	9·3
80°	0·5234	16·10	9·93	9·87	9·9
85°	0·5174	8·05	10·25	10·23	10·2
90°	0·5154	0	10·35	10·35	10·3

$\log a=0·59226$, $\log C_E=0·83103$, $\log C_D=0·76410$.

Differentiating, namely, z with respect to α we have

$$\frac{dz}{d\alpha}=-\frac{dr}{d\alpha}\left(\frac{r}{\sqrt{r^2-a^2}}-1\right),$$

$$\frac{d^2z}{d\alpha^2}=-\frac{d^2r}{d\alpha^2}\left(\frac{r}{\sqrt{r^2-a^2}}-1\right)+\left(\frac{dr}{d\alpha}\right)^2\frac{a^2}{(r^2-a^2)^{3/2}}.$$

By Einstein's formula, then,

$$r=C_E\frac{1}{\sin\alpha\sqrt{\sin^2\alpha-\sin^2\alpha_0}},$$

$$\frac{dr}{d\alpha}=-C_E\cos\alpha\left\{\frac{1}{\sin^2\alpha\sqrt{\sin^2\alpha-\sin^2\alpha_0}}+\frac{1}{(\sin^2\alpha-\sin^2\alpha_0)^{3/2}}\right\},$$

and

$$\frac{d^2r}{d\alpha^2}=C_E\left\{\frac{\sin^2\alpha+2\cos^2\alpha}{\sin^3\alpha\sqrt{\sin^2\alpha-\sin^2\alpha_0}}+\frac{1}{\sin\alpha(\sin^2\alpha-\sin^2\alpha_0)^{3/2}}\right.$$
$$\left.+\frac{3\sin\alpha\cos^2\alpha}{(\sin^2\alpha-\sin^2\alpha_0)^{5/2}}\right\}.$$

Hence, when α is very near α_0, or r very large,

$$\frac{dz}{d\alpha}\doteq-\frac{dr}{d\alpha}\frac{a^2}{2r^2}=\frac{a^2}{2C_E}\cos\alpha\left\{\sqrt{\sin^3\alpha-\sin^2\alpha_0}\right.$$
$$\left.+\frac{\sin^2\alpha}{\sqrt{\sin^2\alpha-\sin^2\alpha_0}}\right\}.$$

Thus, according to Einstein's formula we see, as above mentioned, that $\frac{1}{R}\frac{dz}{d\alpha}$, the tangent of the inclination of the curve traced by the β-particles against the undeflected line on the photographic film becomes positively infinite for $\alpha=\alpha_0$ (provided, of course, $\alpha_0=\sin^{-1}\beta_0$ is not zero, and R, the radius of the film-circle, is finite, both of which were actually fulfilled in Bucherer's experiments, R having been equal to about 8 cm.).

By a similar step we have

$$\frac{1}{R^2}\frac{d^2z}{d\alpha^2}\doteq-\frac{a^2}{2C_ER^2}\frac{\sin^3\alpha\cos^2\alpha}{(\sin^2\alpha-\sin^2\alpha_0)^{3/2}}.$$

The last expression is negatively infinite for $\alpha=\alpha_0$, showing that the curve is concave towards the undeflected line at its vanishing ends ; and it remains as such up to the point of maximum deflexion.

With the writer's formula, on the other hand,

$$r=C_D\frac{1}{\sin^2\alpha-\sin^2\alpha_0},$$

$$\frac{dr}{d\alpha}=-C_D\frac{2\sin\alpha\cos\alpha}{(\sin^2\alpha-\sin^2\alpha_0)^2},$$

and

$$\frac{d^2r}{d\alpha^2}=2C_D\left\{-\frac{\cos^2\alpha-\sin^2\alpha}{(\sin^2\alpha-\sin^2\alpha_0)^2}+\frac{4\sin^2\alpha\cos^2\alpha}{(\sin^2\alpha-\sin^2\alpha_0)^3}\right\}.$$

Hence

$$\left[\frac{dz}{d\alpha}\right]_{\alpha=\alpha_0}=\left[\frac{a^2}{2C_D}\frac{2\sin\alpha\cos\alpha}{(\sin^2\alpha-\sin^2\alpha_0)^2}\cdot(\sin^2\alpha-\sin^2\alpha_0)^2\right]_{\alpha=\alpha_0}$$

$$=\frac{a^2}{2C_D}\sin 2\alpha_0\,;$$

or, $\left[\frac{dz}{R\,d\alpha}\right]_{\alpha=\alpha_0}=\frac{a^2}{2RC_D}\sin 2\alpha_0$, which is approximately equal to 0·099 for Bucherer's experiment No. 15, while the photographic curve near its vanishing ends is seen to be elevated by about 1 mm. against 1 cm. of the zero-line.

Next,

$$\frac{d^2z}{d\alpha^2}=-\frac{d^2r}{d\alpha^2}\left(\frac{r}{\sqrt{r^2-a^2}}-1\right)+\left(\frac{dr}{d\alpha}\right)^2\frac{a^2}{(r^2-a^2)^{3/2}},$$

which becomes approximately, as α approaches α_0, equal to

$$-\frac{a^2}{2}\frac{d^2r}{d\alpha^2}\frac{1}{r^2}+a^2\left(\frac{dr}{d\alpha}\right)^2\frac{1}{r^3}$$

$$=\frac{a^2}{C_D}(\cos^2\alpha-\sin^2\alpha).$$

Thus,

$$\left[\frac{d^2z}{R^2d\alpha^2}\right]_{\alpha=\alpha_0}=\frac{a^2}{R^2C_D}\cos 2\alpha_0.$$

This last expression for $\frac{d^2z}{R^2d\alpha^2}$ is positive as long as α_0 lies between 0 and $\frac{\pi}{4}$, corresponding to the range of $\sin\alpha_0$ from 0 up to 0·7071. But $\sin\alpha_0$ corresponds, in its turn, to the velocity of the β-particles that undergo the maximum deflexion. In Bucherer's experiments it varied between 0·3173 and 0·6870, thus having been included within the above-mentioned range. According to the writer's theory, therefore, his photographic curves are all expected to be convex, contrary to what is claimed by Einstein's theory, near their vanishing ends towards the undeflected line. And at about $\alpha=\frac{\pi}{4}$ * there is expected a point of inflexion, where the curve turns its concavity to the opposite sense.

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[*] This is, of course, an approximate value, $\left(\frac{a}{r}\right)^2$ and smaller quantities being neglected against unity. The magnitude of $\left(\frac{a}{r}\right)^2$ for $\alpha=\frac{\pi}{4}$ is, then, of the order: 0·057 (Exper. No. 7),
0·025 (Exper. No. 15).

As a matter of fact, then, a glancing inspection of Bucherer's photographic curves will be enough to appreciate that just apparently what is described above is actually exhibited in them.

To see the agreement and disagreement in a more contrasted manner, the theoretical data given in Tables I. and II. were plotted in five-fold magnification on a sheet of section paper. The theoretical curves obtained thus tracing through the plotted points were photographically reduced to their proper scale (Pl. VI. fig. 2). Then both the theoretical and Bucherer's experimental curves were at once fixed positively on the dry plates instead of on the developing paper. With these positive plates put together in pairs, and by means of an enlargement-apparatus, the negative plates were made for the theoretical curves superposed upon the experimental ones (Pl. VI. figs. 3 and 4).

4. *Additional Remarks.*

In the above discussion every β-particle has been regarded as confined all over its path within a vertical plane determined by its initial direction of motion. Strictly speaking, however, the particle begins to deviate from that vertical plane under the action of the magnetic field at work, as soon as, after leaving the condenser plates, the vertical component of its velocity comes into existence. Only, the deviation of the sort did not amount in Bucherer's experiments to anything of such importance as to need being taken into consideration in the above discussion.

For the intensity of this disturbing action must be equal to $ev \sin\phi \, H \cos\alpha$, in which $v \sin\phi$ stands for the vertical component of the velocity at the instant under consideration (see fig. 1). In the first approximation we may treat α as a constant, and denoting by ξ the amount of deviation we have

$$m\frac{d^2\xi}{dt^2} = ev \sin\phi H \cos\alpha.$$

But evidently $v = r\dfrac{d\phi}{dt}$, so that

$$m\frac{d^2\xi}{dt^2} = erH \cos\alpha \, . \sin\phi \frac{d\phi}{dt}.$$

Hence,

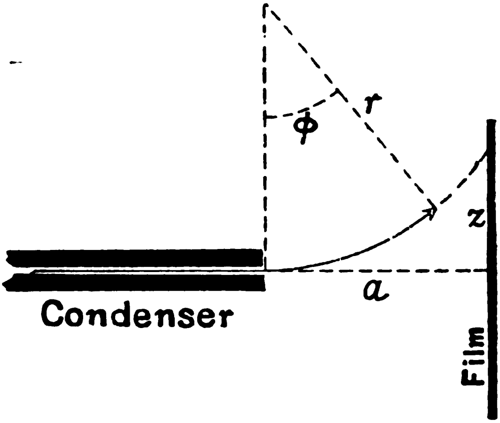
$$m\frac{d\xi}{dt} = -erH \cos\alpha \, . \cos\phi + \text{const.}$$

The condition $\frac{d\xi}{dt}=0$ for $\phi=0$ determines the constant of integration in the last equation, and we have

$$m\frac{d\xi}{dt}=er\text{H}\cos\alpha(1-\cos\phi)$$
$$=\frac{er^2\text{H}\cos\alpha}{v}\left(\frac{d\phi}{dt}-\cos\phi\frac{d\phi}{dt}\right),$$

making use of $v=r\frac{d\phi}{dt}$ once more.

Fig. 1.



Hence, further

$$m\xi=\frac{er^2\text{H}\cos\alpha}{v}(\phi-\sin\phi)+\text{const.}$$

But $\xi=0$ for $\phi=0$, so that finally

$$\xi=\frac{e}{m}\cdot\frac{r^2\text{H}\cos\alpha}{v}(\phi-\sin\phi).$$

By a similar process the expression for z can be derived as

$$z=\frac{e}{m}\cdot\frac{r^2\text{H}\sin\alpha}{v}(1-\cos\phi)^*.$$

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* Putting $\cos\phi=\frac{\sqrt{r^2-a^2}}{r}$, we have indeed

$$z=\frac{e}{m}\cdot\frac{r\text{H}\sin\alpha}{v}(r-\sqrt{r^2-a^2}),$$

which is the combination of equations (2) and (4) p. 435 above.

Thus

$$\xi = z \cot \alpha \frac{\phi - \sin \phi}{1 - \cos \phi}.$$

For the particle arriving at the film,

$$\sin \phi = \frac{a}{r},$$

$$\cos \phi = \sqrt{1 - \left(\frac{a}{r}\right)^2} = 1 - \frac{1}{2}\left(\frac{a}{r}\right)^2 - \frac{1}{8}\left(\frac{a}{r}\right)^4 + \ldots\ldots$$

and $\phi = \sin^{-1}\frac{a}{r} = \frac{a}{r} + \frac{1}{2}\cdot\frac{1}{3}\left(\frac{a}{r}\right)^3 + \frac{3}{2\,.\,4}\cdot\frac{1}{5}\left(\frac{a}{r}\right)^5 + \ldots\ldots$

Neglecting the small quantities of the order $\left(\frac{a}{r}\right)^2$ against unity we have

$$\xi = \frac{1}{3} z \,.\, \frac{a}{r} \cot \alpha.$$

Referring to the values for ξ given in Table III. (corresponding to Bucherer's experiment No. 15) and the actual appearance of the experimental curve (Pl. VI. fig. 1), it will be seen at once that the general character of the curve is still far from being affected by the deviation so far studied above. Indeed, the greatest value of ξ cannot possibly exceed 0·5 mm., while it is with difficulty that the point where the maximum deflexion is expected, or $\alpha = \frac{\pi}{2}$, is decided exactly to 1 mm. along the zero-line.

Before concluding the present discussion, one more remark should be added here, which bears some importance regarding the examination of Bucherer's experimental results.

He announces in the *Annalen der Physik* that the inner diameter of the cylinder was about 16 cm. round the inside of which the photographic films were extended. The expected distance along the film, therefore, between the two vanishing ends of the photographic curve is:

$$l = 2 \times 8 \text{ cm.} \left(\frac{\pi}{2} - \alpha_0\right)$$

$$= 16 \left(\frac{\pi}{2} - \sin^{-1} \beta_0\right) \text{ cm.}$$

Thus,

$l = 18$ cm., for Exper. No. 7;

and $l = 16·5$ cm., for Exper. No. 15.

TABLE III.—(For Experiment No. 15.)

a.	log cot a.	$\log \frac{a}{r}$.	log z.	$\xi = \frac{1}{3} z \frac{a}{r} \cot a$.
31°......	0·22123	$\bar{2}$·01989	$\overline{\infty}$	0 mm.
35°......	0·15477	$\bar{2}$·63246	$\bar{1}$·92428	0·02
40°......	0·07619	$\bar{2}$·99815	0·29226	0·08
45°......	0·00000	$\bar{1}$·19873	0·49276	0·16
47°......	$\bar{1}$·96966	$\bar{1}$·25889	0·55388	0·20
50°......	$\bar{1}$·92381	$\bar{1}$·33541	0·63144	0·26
52°......	$\bar{1}$·89281	$\bar{1}$·37923	0·67669	0·30
55°......	$\bar{1}$·84523	$\bar{1}$·43640	0·73640	0·35
57°......	$\bar{1}$·81252	1·46973	0·77012	0·38
60°......	$\bar{1}$·76144	$\bar{1}$·51365	0·81690	0·41
62°......	$\bar{1}$·72567	$\bar{1}$·53939	0·84386	0·43
65°......	$\bar{1}$·66867	$\bar{1}$·57332	0·88081	0·44
67°......	$\bar{1}$·62785	1·59312	0·90200	0·44
70°......	$\bar{1}$·56107	$\bar{1}$·61897	0·93044	0·43
75°......	$\bar{1}$·42805	$\bar{1}$·65276	0·96755	0·37
80°......	$\bar{1}$·24632	$\bar{1}$·67608	0·99432	0·28
85°......	$\bar{1}$·94195	1·68977	1·00988	0·15
90°......	$\overline{\infty}$	$\bar{1}$·69429	1·01494	0

Rough estimation of the lengths of Bucherer's photographic curves will show at once that these expected values are far too low. With 8 cm. for the inner radius of the cylinder and the actual lengths of the photographic curves

l = 19·8 cm. (about), for Exper. No. 7,

and l = 19·0 cm. (about), for Exper. No. 15,

we shall have respectively

$$\frac{\pi}{2} - \alpha_0' = 70^\circ{\cdot}9 \text{ instead of } \frac{\pi}{2} - \alpha_0 = 64^\circ{\cdot}65 \text{ (No. 7)},$$

and
$$\frac{\pi}{2} - \alpha_0' = 68^\circ{\cdot}0 \text{ instead of } \frac{\pi}{2} - \alpha_0 = 58^\circ{\cdot}97 \text{ (No. 15)};$$

and consequently

$\beta_0' = 0{\cdot}327$ instead of Bucherer's $\beta_0 = 0{\cdot}4281$ (No. 7),

and $\beta_0' = 0{\cdot}374$ instead of Bucherer's $\beta_0 = 0{\cdot}5154$ (No. 15).

Now, it may be too far here to enter into any speculative inquiry as to what disturbing cause should have given rise to the above-mentioned discrepancies. And yet it may be noticed, all the same, that some systematic or other error must have anyhow been inherent to Bucherer's estimation of the effective field-intensities at work. Whether the terminal voltage applied to the condenser plates may have suffered a drop due to the current, if it were ever so feeble, flowing between the plates, cannot be said positively.

At any rate, it is preferable, it may dare be said however, not to evaluate the absolute value of $\frac{e}{m}$ for small velocities from Bucherer's experimental data, and the writer is inclined to stop at, and not to go any further from, regarding the very high merit of the experiments as lying in an elegant photographic representation of the general character of the velocity-function for $\frac{e}{m}$. It is sufficient for us by itself alone to distinguish decisively between the different theories of the constitution of the electron.

For the absolute value of $\frac{e}{m}$ for small velocities, then, we had better turn with Sommerfeld [*] to another region of our experimental knowledge. From the universally accepted constant of electrolysis we have,

$$\frac{e}{m_H}=2{\cdot}872\times10^{14}\text{ e.s.u.};$$

and the recently obtained spectroscopic data of the hydrogen and helium Balmer series enable us with the help of Bohr's theory to estimate

$$\frac{m_H}{m}=1847.$$

Thus the value of $\frac{e}{m}$ for small velocities is determined, to a sufficient degree of accuracy, to be

$$\frac{e_0}{m_0}=5{\cdot}305\times10^{17}\text{ e.s.u.},$$

and $$=1{\cdot}769\times10^{7}\text{ e.m.u.},$$

the value that is most reliable at present.

Physical Institute, Faculty of Science,
Imperial University of Tokyo, Japan,
June 1924.

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[*] A. Sommerfeld, *Atombau und Spektrallinien*, 3rd edition, p. 272.

XLV. *On the Stabilization of Instable Equilibrium by means of Gyroscopic Forces.* *By* Dr. H. J. E. Beth (*Deventer*)[*].

THOMSON and Tait have[†] investigated the equilibrium of a dynamical system when, besides forces deriving from a force function, gyroscopic forces are working on the system. An important part of the results they arrived at may be expressed in this manner:—If the number of the instabilities which the system possesses (taking away the gyroscopic forces) is an odd number, it is impossible to stabilize the equilibrium by the means of gyroscopic forces. Moreover, several examples are treated of instable equilibrium with an even number of instabilities where stabilization by the means of such forces appeared to be possible. The general observation was made that the gyroscopic forces will dominate if they become of sufficient greatness.

In this paper I will prove that stabilization of instable equilibrium with an even number of instabilities by means of gyroscopic forces is *always* possible, and I will derive the conditions which must be fulfilled by those forces[‡].

We start from the determinantal equation

$$D \equiv \begin{vmatrix} m^2+a_{11} & a_{12}m & a_{13}m \ldots\ldots\ldots & a_{1n}m \\ -a_{12}m & m^2+a_{22} & a_{23}m \ldots\ldots\ldots & a_{2n}m \\ -a_{13}m & -a_{23}m & m^2+a_{33} \ldots\ldots\ldots & a_{3n}m \\ \vdots & \vdots & \vdots & \vdots \\ -a_{1n}m & -a_{2n}m & -a_{3n}m \ldots\ldots & m^2+a_{nn} \end{vmatrix} = 0 \;. \qquad (1)$$

for a mechanism having n degrees of freedom.

The coefficients $a_{11}, a_{22} \ldots . a_{nn}$ arise from the potential energy, the coefficients a_{12}, a_{13}, etc. from the gyroscopic forces. If all gyroscopic coefficients are zero, the equation (1) passes into

$$(m^2+a_{11})(m^2+a_{22}) \ldots\ldots\ldots (m^2+a_{nn})=0.$$

Now we suppose the equilibrium without gyroscopic forces to be instable; therefore not all coefficients a_{11}, $a_{22} \ldots\ldots a_{nn}$ are positive. We may suppose an even number l of them to be negative.

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[*] Communicated by the Author.

[†] 'A Treatise of Natural Philosophy,' i. p. 391, etc.

[‡] The question was set by the Mathematical Society of Amsterdam for the year 1923.

Therefore in the equation

$$D \equiv \begin{vmatrix} m_2+a_{11} & a_{12}m \ldots\ldots\ldots & a_{1l}m \ldots\ldots\ldots & a_{1n}m \\ -a_{12}m & m^2+a_{22} \ldots\ldots\ldots & a_{2l}m \ldots\ldots\ldots & a_{2n}m \\ -a_{13}m & -a_{23}m \ldots\ldots\ldots & a_{3l}m \ldots\ldots\ldots & a_{3n}m \\ \vdots & \vdots & \vdots & \vdots \\ -a_{1l}m & -a_{2l}m \ldots\ldots\ldots & m^2+a_{ll} \ldots\ldots\ldots & a_{ln}m \\ -a_{1,l+1}m & -a_{2,l+1}m & \ldots\ldots\ldots\ldots\ldots\ldots & a_{l+1,n}m \\ \vdots & & & \\ -a_{1n}m & -a_{2n}m & \ldots\ldots\ldots\ldots\ldots\ldots & m^2+a_{nn} \end{vmatrix} = 0$$

the coefficients $a_{11}, a_{22} \ldots\ldots a_{ll}$ are negative, $a_{l+1,l+1} \ldots\ldots a_{nn}$ are positive. We will prove that it is possible to choose the values of the coefficients $a_{12}, a_{13} \ldots\ldots$ in such a way that the equation $D=0$ has its roots negative.

We take for this purpose

$$\begin{array}{lll} a_{1,l+1}=0, & a_{2,l+1}=0, \ldots\ldots\ldots & a_{l+1,n}=0, \\ a_{1,l+2}=0, & a_{2,l+2}=0, & a_{l+2,n}=0, \\ \vdots & & \\ a_{1n}=0, & a_{2n}=0, & a_{nn}=0, \end{array}$$

by which the equation passes into

$$D \equiv (m^2+a_{l+1,l+1}) \ldots\ldots (m^2+a_{nn}) \begin{vmatrix} m^2+a_{11} & a_{12}m \ldots\ldots\ldots & a_{1l}m \\ -a_{12}m & m^2+a_{22} \ldots\ldots & a_{2l}m \\ \vdots & \vdots & \vdots \\ -a_{1l}m & -a_{2l}m & m^2+a_{ll} \end{vmatrix} = 0.$$

Of the equation $D=0$, $n-l$ roots m^2 are equal to $-a_{l+1,l+1}$, $-a_{l+2,l+2}, \ldots\ldots, -a_{nn}$, which roots are negative; from this it follows that the $n-l$ stabilities are maintained.

The system of n degrees of freedom with partial stability has now been reduced to a system of l degrees of freedom, possessing only instabilities. Its determinantal equation

$$\Delta \equiv \begin{vmatrix} m^2+a_{11} & a_{12}m \ldots\ldots\ldots & a_{1l}m \\ -a_{12}m & m^2+a_{22} \ldots\ldots\ldots & a_{2l}m \\ \vdots & \vdots & \vdots \\ -a_{1l}m & -a_{2l}m \ldots\ldots & m^2+a_{ll} \end{vmatrix} = 0 \quad . \quad . \quad (2)$$

contains the l remaining roots m^2. We have to prove still that the coefficients $a_{12}, a_{13} \ldots\ldots$ may be chosen in such a way that the equation $\Delta=0$ has its roots negative ; $a_{11}, a_{22} \ldots\ldots a_{ll}$ are all negative.

We put

$$m=\frac{m'}{\lambda}, \qquad a_{12}=\frac{c_{12}}{\lambda} \ldots\ldots a_{l-1,l}=\frac{c_{l-1,l}}{\lambda},$$

λ being a parameter. The equation passes into

$$\begin{vmatrix} m'^2+a_{11}\lambda^2 & c_{12}m' \ldots\ldots\ldots & c_{1l}m' \\ -c_{12}m' & m'^2+a_{22}\lambda^2 \ldots\ldots & c_{2l}m' \\ \vdots & \vdots & \vdots \\ -c_{1l}m' & -c_{2l}m' \ldots\ldots & m'^2+a_{ll}\lambda^2 \end{vmatrix}=0. \quad . \quad (3)$$

Now we suppose

$$|\,a_{ik}\,| \neq 0 \qquad (a_{ik}=-a_{ki},\ a_{kk}=0), \quad . \quad . \quad . \quad . \quad (4)$$

and therefore

$$|\,c_{ik}\,| \neq 0 \qquad (c_{ik}=-c_{ki},\ c_{kk}=0). \quad . \quad . \quad . \quad . \quad (4a)$$

When λ approaches zero the roots may be divided into two classes: those of the second class approach to a finite limit different from zero ; those of the first class approach zero, and the ratios of one of the roots and λ^4 is different from zero.

The roots m'^2 of the second class are given by

$$d \equiv \begin{vmatrix} m' & c_{12} \ldots\ldots\ldots & c_{1l} \\ -c_{12} & m' \ldots\ldots\ldots & c_{2l} \\ \cdots\cdots & \cdots\cdots\cdots & \cdots\cdots \\ -c_{1l} & -c_{2l} \ldots\ldots\ldots & m' \end{vmatrix}=0. \quad . \quad . \quad (5)$$

In order to obtain the remaining roots m^2, we substitute in (3) $m'=\frac{\lambda^2}{m''}$; the equation passes into

$$\begin{vmatrix} \lambda^2+a_{11}m''^2 & c_{12}m'' & \ldots\ldots & c_{1l}m'' \\ -c_{12}m'' & \lambda^2+a_{22}m''^2 & \ldots\ldots & c_{2l}m'' \\ \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\ -c_{1l}m'' & -c_{2l}m'' & \ldots\ldots & \lambda^2+a_{ll}m''^2 \end{vmatrix}=0,$$

which equation has $\frac{1}{2}l$ roots m''^2 of moderate value, and $\frac{1}{2}l$ roots of order λ^4. The roots of the first class are approximately given by

$$\begin{vmatrix} a_{11}m'' & c_{12} & \dots\dots & c_{1l} \\ -c_{12} & a_{22}m'' & \dots\dots & c_{2l} \\ \dots & \dots & \dots & \dots \\ -c_{1l} & -c_{2l} & \dots\dots & a_{ll}m'' \end{vmatrix} = 0. \quad . \quad . \quad . \quad (6)$$

The roots m''^2 of this equation have the sign of those roots m'^2 of (3), which are not given by (5). We therefore have to prove that the roots m'^2 of (5) and the roots m''^2 of (6) are all negative if the coefficients a_{12}, a_{13} ...... have been chosen well.

In the first place we prove that the roots m'^2 of (5) are negative provided the condition (4 *a*) is fulfilled. For this purpose we start from (3) with the supposition that a_{11}, a_{22} ...... a_{ll} are all positive. It is a well-known fact that in this case all roots of m'^2 of (2) are negative * (it is the analytical expression of the fact that stable equilibrium may never be lost by gyroscopic forces). The proposition holds good for small values of λ. If $\lambda=0$, $\frac{1}{2}l$ roots m'^2 become zero, and the other remain negative; these roots, however, are given by (5).

In the second place we prove that with the same condition the roots m''^2 of (6) are negative. If we substitute

$$a_{11}=-a_{11}', \; a_{22}=-a_{22}' \; \dots\dots \; a_{ll}=-a_{ll}',$$

we may also write (6)

$$\begin{vmatrix} a_{11}'m'' & c_{12} & \dots\dots & c_{1l} \\ -c_{12} & a_{22}'m'' & \dots\dots & c_{2l} \\ \dots & \dots & \dots & \dots \\ -c_{1l} & -c_{2l} & \dots\dots & a_{ll}'m'' \end{vmatrix} = 0.$$

When we divide the elements of the first row and those of the first column by $\sqrt{a_{11}'}$, those of the second row and of the second column by $\sqrt{a_{22}'}$, and so on, then a determinantal equation arises in the shape of (5) with other values of the c; however, the new c fulfil the condition (4 *a*); so the roots m''^2 of (6) are negative.

Therefore stabilization may always be obtained by values of a_{12}, a_{13} ......, which are of sufficient greatness and which fulfil the inequality (4).

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* A proof is to be found in Routh, 'Stability of Motion,' p. 77.

XLVI. *On the Impact with Liquid Surfaces of Solid Bodies of Various Shapes.* By G. ERIC BELL, *B.Sc., Physics Research Laboratory, University College, Nottingham* *.

[Plate VII.]

IN a previous paper † the author discussed in some detail the phenomena attending the impact of solid spheres with fluid surfaces, and showed that they were dependent on

(1) The surface tension of the liquid;
(2) The viscosity of the liquid;
(3) The condition of the surface of the body.

As was previously observed by Worthington ‡, this last factor is by far the most important. In the present paper an account is given of research on the impact of solid bodies with liquids, with particular reference to the shape of the bodies.

The research was carried out with exactly the same apparatus as the previous work, and in exactly the same manner. Shadow photographs were obtained showing the state of the body and liquid at various short intervals of time after the impact, a typical selection of which is reproduced in Pl. VII.

In all these photographs the height of fall is such that the velocity of the body on entering the liquid is of the order 250 cm. per sec.

In the first series of photographs, Pl. VII. fig. 1 (*a*, *b*, & *c*), a cylinder of length 4·4 cm. and diameter 0·8 cm. was allowed to fall into water, the surface of the cylinder being first carefully cleaned and polished. The same cylinder was then again cleaned and polished, and coated thinly with a layer of paraffin oil, giving the results shown in fig. 2 (*a*, *b*, & *c*). Throughout all these experiments, the photographs obtained with a surface coated with paraffin oil may be regarded as typical of the general effects of coating the body with a layer of a substance of low surface-tension. Many such substances were tried, such as various oils, turpentine, and alcohol, and the photographs only differ in minute details not considered for the present purpose.

In the series shown in figs. 3 (*a*, *b*, & *c*) and 4 (*a*, *b*, & *c*) the process was repeated, using a cylinder 3·15 cm. long and 0·56 cm. diameter. The similarity between the photographs for the large cylinder and the small one is very striking. (Fig. 1 is to be compared with fig. 3, and fig. 2 with fig. 4.) This is true throughout all the photographs taken.

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* Communicated by Prof. E. H. Barton, D.Sc., F.R.S.

† Phil. Mag. xlviii. p. 753 (November 1924).

‡ Phil. Trans. Roy. Soc. A, cxciii. (1897) and A, ccxxv. (1900).

One end of each cylinder was then turned hemispherical, and the resulting body polished, and another two series of photographs taken. Typical examples are shown in figs. 5 (*a*, *b*, & *c*) and 6 (*a*, *b*, & *c*), the surface being clean in the first case, soiled in the second.

The other end of each cylinder was then turned hemispherical, giving a body hemispherical at each end, and other photographs taken, giving the results shown in figs. 7 (*a*, *b*, & *c*) and 8 (*a*, *b*, & *c*).

Finally, the impact of a body pointed at one end and hemispherical at the other was studied, the result being shown in figs. 9 (*a*, *b*, & *c*) and 10 (*a*, *b*, & *c*).

The three photographs of fig. 11 may be considered as typical of the phenomena occurring when a body is allowed to fall into a liquid of low surface-tension—in this particular case turpentine.

Analysis of the Photographs.

It will be seen from the reproductions in Pl. VII. that when a perfectly clean cylinder is allowed to fall into water, there is a considerable disturbance in the liquid, and a large air-cavity of considerable size and curious shape is produced. The most noteworthy point about this air-cavity is that it closes up very rapidly at the mouth. The actual disturbance at the surface itself is very slight; if, however, the same cylinder is coated with paraffin oil, a considerable surface-disturbance occurs, and the tendency of the air-cavity to close in at the surface disappears: the cavity continues to get wider right to the surface. It will further be noticed that the basin-like surface-disturbance is completely formed almost as soon as the end of the cylinder penetrates the liquid-surface.

Turning to the case when the end of the cylinder is made hemispherical and the surface clean, we observe that the body penetrates the surface with no disturbance—a phenomenon observed by Worthington (*loc. cit.*) for a sphere falling slowly. There is this difference, however, that while a sphere under conditions of comparatively low impact-velocity makes no air-cavity, the cylinder draws after it a long, nearly cylindrical cavity. The difference in shape between this cavity and that produced by a sphere (described in the previous paper) is very remarkable. This particular type of splash seems to be the counterpart for an elongated body with a hemispherical nose and flat top of the "smooth" splash caused by spherical bodies.

Again, if the surface is coated with paraffin oil (or other oil), a pronounced surface-disturbance makes its appearance, and the air-cavity forms a neck.

A body which is round at both ends, and clean, penetrates the surface without disturbance, and the liquid closes over the top without drawing after it an air-cavity. We have, in fact, a "smooth" splash. When this body is coated with paraffin oil, it makes a disturbance of exactly the same kind as that caused by a body rounded at one end only.

A body which is pointed at one end produces a "smooth" splash, whether its surface is clean or coated with an oil-film. The body used in this case is not so highly polished as in the previous cases, and a small air-bubble adheres to its upper surface, which shows ripple-marks.

Explanation of the Results.

These observations may be summarized as follows:—

(1) A pronounced surface-disturbance never appears when the bodies used are clean and free from surface-films, and the liquid into which they fall has a high surface-tension, provided that the height of fall is not too great.

(2) The surface-disturbance, if any, is produced by the nose immediately after penetration.

(3) The pointed body used does not produce an air-cavity and surface-disturbance, even if its surface is coated with an oil-film, for these impact-velocities.

(4) An air-cavity is produced by a blunt nose. This cavity remains open if the surface of the body is contaminated, but rapidly closes if the surface is clean.

(5) An air-cavity is drawn down if the upper end of the body is flat; this cavity remains nearly cylindrical if the body is clean, but assumes a different form if the body is coated with an oil-film.

These various phenomena receive an explanation, at least qualitatively, by considering the forces acting on an element of the fluid in contact with the impinging body. We may consider three such forces :—

(1) A force F, tending to cause the liquid to flow horizontally outwards with a certain velocity. This force may be considered as constant for any given body, whatever the state of its surface; it is a function of the velocity only.

(2) The force due to surface-tension round the boundary of the liquid in contact with the body. The result is a force, say AT, normally inwards, A being a constant.

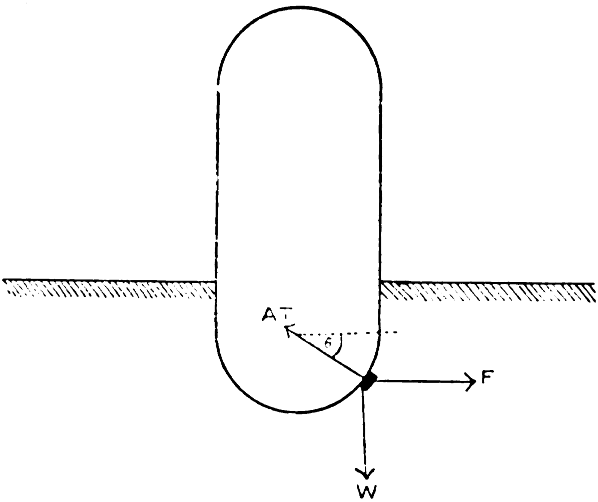
(3) A force P, normally inwards, due to hydrostatic pressure. As we shall only consider the effects immediately after impact, and near the surface, this may be neglected.

(4) The weight of the liquid acting vertically downwards, of magnitude, say, W.

The Surface Disturbance.

Consider the forces acting on a small prism of the liquid, one face of which is in contact with the body.

Fig. 1.



The various forces act as shown in fig. 1. Consider the special case of a body with a hemispherical end, and take spherical coordinates, of which the origin is the centre of the hemisphere. Let the coordinates of the portion of liquid considered be $(r, \theta, 0)$.

Then the horizontal force tending to draw the liquid away from the solid surface is given by

$$F - AT\cos\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the vertical force urging the liquid upwards is

$$AT\sin\theta - W. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The equations cannot be expected to hold for $\theta = \frac{\pi}{2}$, because the forces will not have had time to be established, and also because the area of cross-section of the body immersed in the liquid will be very small.

From equation (1) we see that the force tending to draw the liquid away from the body is greater if the surface-tension is reduced. Hence, if a liquid of low surface-tension is used, or if the body is coated with a layer of a liquid of low surface-tension, the cavity should form more easily—which the photographs show to be the case. Further, an increase in the height of fall, which increases F, tends to cause an open air-cavity to form. It is also apparent from equation (1) that the cavity, if formed at all, will be formed very soon after impact, when $\cos\theta$ is small, which again is known to be the case.

Further, if the body fall in such a manner that a cavity is formed, it is evident that the liquid has both a horizontal and vertical velocity, which, on account of internal friction etc., will be less for portions of the liquid near to the body than for portions further away. This vertical velocity, which tends to increase the surface of the liquid, will diminish more rapidly if the surface-tension and viscosity of the liquid are greater. Thus, for liquids like water and turpentine, which have viscosities of the same order but very different surface-tensions, the upshot rim should be greater in the case of turpentine, the surface of the body being the same in each case. This is the case, as is shown in figs. 5 and 11 of Pl. VII. of this paper. With increase of viscosity, both the height of the upshot rim and the width of the cavity will be less, as is shown to be the case in the photographs of the previous paper, where glycerine of high viscosity is used as the main liquid.

It further appears from equations (1) and (2) that for high entrance-velocities the horizontal component of the velocity of the liquid will be increased and the vertical component slightly diminished. Thus the upshot rim should be more open at the top for high falls than for low falls. This is experimentally shown to be true in the photographs obtained by Worthington (*loc. cit.*).

Similar considerations hold for the upper end of the body. If it is rounded, there is a resultant force tending to hold the liquid to the surface of the body, and hence cause a "smooth" splash. On the other hand, if the upper surface is flat the liquid leaves the surface, and an air-cavity is produced as shown in fig. 5 of Pl. VII.

The case of the pointed body affords another verification of these principles.

The expression giving the resultant force tending to draw the liquid away from the body, $F - AT\cos\theta$, shows that, if $AT\cos\theta < F$, the liquid clings to the body and no cavity is formed. Now, for a pointed body θ is always of a definite value, and if the point is sharp, $\cos\theta$ is large. Thus the liquid does not easily flow away; figs. 9 and 10 of the plate show that, for the particular body used, $AT\cos\theta$ remains greater than F, even when T is reduced by coating the surface with paraffin oil.

It can be experimentally shown that if the height of fall is increased (thus increasing F), or if the point is made more blunt (thus decreasing $\cos\theta$), a rough splash may be produced.

Summary.

In this paper the splashes caused by bodies of various shapes falling into liquids are discussed. It is shown that the type of splash depends jointly on the shape of the nose of the body and on the state of its surface. A simple scheme is outlined which explains these results qualitatively.

University College, Nottingham,
November 28, 1924.

XLVII. *On Eddington's Natural Unit of the Field, and Possible Relations between it and the Universal Constants of Physics.* By J. RICE, *M.A., Associate-Professor in the Department of Physics, University of Liverpool* *.

IN a paper published three years ago in the 'Proceedings of the Royal Society' † and more recently in his book on Relativity ‡, Professor Eddington has put forward a very attractive hypothesis which he calls the Principle of Identification. He points out that two avenues of scientific investigation initially widely separated have gradually converged: one, the *deductive* study of pure geometry; the other, the *inductive* study of "the physical world consisting of space, time, and things." On the one hand, the geometers have developed a pure geometry, making use of certain tensors which possess definite properties *by virtue of mathematical identities*; on the other hand, the physicists have been led, owing to the rise of the Relativity Principle, to introduce into mathematical physics tensors possessing definite properties *by reason of those generalizations from experiment which we refer to as the laws of conservation of energy and momentum, the laws of the electromagnetic field, and the law of gravitation.*

It appears that in several cases the properties possessed by a geometrical tensor are identical with those possessed by one of the physical tensors. This suggests that if any further advance be made in physical science, conforming presumably to the Principle of Relativity and therefore involving the introduction of fresh tensors in its mathematical formulation, it may be possible to discover geometrical tensors possessing by virtue of identities just the same properties as the newly-introduced physical tensors possess by reason of experimental fact. If we can in general apply with success this "Principle of Identification," we can hardly go further in physical theory. (It is, as Eddington remarks, a problem for the psychologist rather than for the physicist to determine how the mind is cognisant of those physical quantities whose behaviour is so closely simulated by a world of entities constructed out of that relation-structure which is described in pure geometry.) Such an application finds but little favour in certain quarters, where it is described as a "geometrization of physics." It would appear, however, to be just as reasonable to assert that the method is "physicising geometry." In any case, nothing more serious seems to be in question than the apparently innocuous result that the mathematical material most suited to the treatment of the properties of a four-dimensional manifold turns out to be also the most convenient implement for expressing the general principles to which physicists have been led by their own experimental observations.

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* Communicated by the Author.

† Proc. Roy. Soc. A, xcix. pp. 104–123 (May 1921).

‡ 'The Mathematical Theory of Relativity' (Camb. Univ. Press 1923).

One interesting suggestion arising out of this Principle of Identification concerns natural units in which physical quantities may be measured. Supposing we accept the hypothesis put forward by Einstein and de Sitter that space is finite though unbounded; and suppose we also adopt Eddington's view that Einstein's law of gravitation

$$G_{\mu\nu}=\lambda g_{\mu\nu}$$

in an empty region is really a gauging equation which gives to the world all the most important properties of a world of uniform curvature, not because of any innate tendency in the world to this symmetrical form, but because we adapt our natural gauge of length at different points and in different directions to make it so. Then it would seem that the radius of curvature of this world should be the natural unit of length on which the units employed in the geometrical tensors should be based. But if there be an underlying connexion between geometrical and physical tensors, such a fundamental unit of length might conceivably lead to the discovery of natural units in which to measure physical quantities. In fact, in the paper referred to, Eddington has attempted to arrive at a natural unit in which to express the matter-tensor $T_{\mu\nu}$, and the electromagnetic energy-tensor $E_{\mu\nu}$. When expressed in such a unit, it would be reasonable to assume that $T_{\mu\nu}=E_{\mu\nu}$ in an electromagnetic field, while in space containing electrons $T_{\mu\nu}-E_{\mu\nu}$ would represent a tensor corresponding to the non-Maxwellian stresses which preserve the electron from disintegration under the mutual repulsion of its parts. The reasoning in this part of the paper referred to is based on a Hamiltonian variation of the invariant integral

$$\int {}^*G_{\alpha\beta}\,{}^*G^{\beta\alpha}\sqrt{(-g)}\,d\tau,$$

where ${}^*G_{\mu\nu}$ is contracted from the curvature in-tensor ${}^*R^{\kappa}_{\lambda\mu\nu}$, and $d\tau$ is the element of four-dimensional space.

In what follows, the writer attempts to arrive at Eddington's conclusions in a different and possibly more direct manner.

The in-tensor $*G_{\mu\nu}$ resolves itself naturally into two parts, a symmetric tensor $R_{\mu\nu}$ and an anti-symmetric tensor $F_{\mu\nu}$. Now consider a system of coordinates in which the unit-mesh has a width $\lambda^{-\frac{1}{2}}$ cm., where λ cm.$^{-2}$ is the world curvature. This means that observers considering the local part of the world as referred to a Galilean system of coordinates will regard two points on the x_μ axis at a distance apart of 1 cm. as having a δx_μ equal to $\lambda^{\frac{1}{2}}$. Let us also use the length $\lambda^{-\frac{1}{2}}$ cm. as a gauge. Such a gauge-coordinate system could plausibly be taken as fundamental in so far as determination of the units of physical magnitude is concerned; not, of course, in any sense in which it could be considered as privileged, for that would violate the Relativity Principle.

Now in such a gauge-coordinate system the metric tensor $g_{\mu\nu}$ is simply given by

$$R_{\mu\nu} = g_{\mu\nu}.$$

From $g_{\mu\nu}$ we construct, as usual, the Christoffel indices $\{\lambda\mu, \nu\}$, and thence the Riemannian curvature tensor $R^{\epsilon}_{\lambda\mu\nu}$ and the Einstein tensor $G_{\mu\nu}$. We can write

$$R_{\mu\nu} = G_{\mu\nu} + H_{\mu\nu},$$

where $H_{\mu\nu}$ is a symmetric tensor, which Eddington surmises is connected in some way not yet explained with the non-Maxwellian binding stresses on the electron. But we have no further concern with $H_{\mu\nu}$ here.

In this coordinate-gauge system the matter-tensor is identified with

$$G_\mu^{\ \nu} - \tfrac{1}{2} g_\mu^{\ \nu}(G - 2). \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

The electromagnetic energy-tensor is identified with

$$F_{\mu\alpha} F^{\nu\alpha} - \tfrac{1}{4} g_\mu^{\ \nu} F_{\alpha\beta} F^{\alpha\beta}. \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

A certain similarity in their construction appears if we write (1) in the form

$$R_{\mu\alpha} G^{\nu\alpha} - \tfrac{1}{2} g_\mu^{\ \nu}(R_{\alpha\beta} G^{\alpha\beta} - 2),$$

which is true since $R_{\mu\nu} = g_{\mu\nu}$. Making the plausible assumption that the physical tensors which have been so identified with the geometrical tensors (1) and (2) are in this gauge system expressed in the same unit, we can then say that in an electromagnetic field

$$G_\mu^{\ \nu} - \tfrac{1}{2} g_\mu^{\ \nu}(G - 2) = F_{\mu\alpha} F^{\nu\alpha} - \tfrac{1}{4} g_\mu^{\ \nu} F_{\alpha\beta} F^{\alpha\beta}. \quad . \quad . \quad . \qquad (3)$$

Let us now transform to a system in which the gauge is one centimetre, and in which a local Galilean frame will make the coordinate difference for two points one centimetre apart on an axis equal to unity. If accented symbols are used for this system, we have

$$R_{\alpha\beta}\delta x_\alpha \delta x_\beta = R'_{\alpha\beta}\delta x'_\alpha \delta x'_\beta,$$

for $R_{\mu\nu}$ is an in-tensor, and so $R_{\alpha\beta}\delta x_\alpha \delta x_\beta$ is an invariant.

As $\delta x'_\mu = \lambda^{-\frac{1}{2}}\delta x_\mu$, it follows that

$$R'_{\mu\nu} = \lambda R_{\mu\nu}.$$

But in this gauge-coordinate system we know that

$$R'_{\mu\nu} = \lambda g'_{\mu\nu}.$$

Hence

$$g'_{\mu\nu} = g_{\mu\nu}.$$

Since λ is a constant, it appears on considering the manner by which the $G'_{\mu\nu}$ are constructed from the $g'_{\mu\nu}$ and their differential-coefficients that

$$G'_{\mu\nu} = \lambda G_{\mu\nu}.$$

As $F_{\mu\nu}$ is an in-tensor, it follows, as in the case of $R_{\mu\nu}$, that

$$F'_{\mu\nu} = \lambda F_{\mu\nu}$$

and therefore

$$H'_{\mu\nu} = \lambda H_{\mu\nu}.$$

It is also true (since $g'_{\mu\nu} = g_{\mu\nu}$) that

$$G'^{\mu\nu} = \lambda G^{\mu\nu},$$

$$G'^{\nu}_{\mu} = \lambda G^{\nu}_{\mu},$$

and

$$G' = \lambda G.$$

Hence, by (3),

$$F_{\lambda\alpha}F^{\mu\alpha} - \tfrac{1}{4}g^{\nu}_{\mu}F_{\alpha\beta}F^{\alpha\beta} = \lambda^{-1}[G'^{\nu}_{\mu} - \tfrac{1}{2}g'^{\nu}_{\mu}(G' - 2\lambda)].$$

The left-hand side of this equation is $-E^{\nu}_{\mu}$ where E^{ν}_{μ} is the electromagnetic energy-tensor, *the field-components being expressed in Eddington's natural field-unit.* By the law of gravitation

$$G'^{\nu}_{\mu} - \tfrac{1}{2}g'^{\nu}_{\mu}(G' - 2\lambda) = -8\pi\kappa T'^{\nu}_{\mu},$$

where T'^{ν}_{μ} is the matter-tensor *expressed in* C.G.S. *units* (*i. e.*, units in which the mass-density arising from the component T'^{44} of the contravariant tensor is in grams per c.c.), and κ is the quotient of the astronomical constant by the square of the velocity of light (approximately $7{\cdot}4 \times 10^{-29}$ in C.G.S. units).

Hence

$$E_\mu{}^\nu = 8\pi\kappa\lambda^{-1} T'_\mu{}^\nu,$$

and in particular

$$E_4{}^4 = 8\pi\kappa\lambda^{-1} T'_4{}^4. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $E_4{}^4 = \frac{1}{2}(e^2 + h^2)$, e and h being the values of the electric and magnetic intensities of the field *in natural units*.

Consider an electrostatic field whose intensity is 1 natural-unit, so that $e=1$, $h=0$; let its value be b electrostatic units; the energy-density of this field is $b^2/8\pi$ ergs per c.c., and therefore

$$T'_4{}^4 = b^2/8\pi c^2,$$

where c is the velocity of light. Hence by (4)

$$\tfrac{1}{2} = 8\pi\kappa\lambda^{-1} b^2/8\pi c^2;$$

$$\text{i.e.,} \quad b = c\sqrt{(\lambda/2\kappa)},$$

or the natural unit of field is

$$c\sqrt{(\lambda/2\kappa)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in electrostatic units.

In the paper quoted, Eddington assumes λ to be of the order 10^{-50}, taking the radius of curvature of the world to be of the order 10^7 parsecs (3×10^{25} cm.). This makes the natural field-unit of the same order as the electrostatic unit of field. Lately, however, opinion seems to be tending to a much smaller value for the curvature. Thus de Sitter and Shapley estimate values for the radius of curvature approaching 10^{10} parsecs, while in a recent communication to 'Nature' (March 8 and April 26, 1924) Silberstein suggests a value as high as 5×10^{12} parsecs. If we take Silberstein's value, making λ of the order 10^{-62}, it gives us less than a millionth of an electrostatic unit as the order of magnitude of Eddington's natural field-unit.

From this unit field it is easy to obtain natural units for other physical quantities, and it is interesting to speculate on a possible connexion between such units and the universal constants of physical science. Thus, if we denote the radius of curvature of the world by R, we can introduce a "cosmic" unit of electric charge (to use Weyl's term). Representing this unit by ϵ ordinary units (electrostatic), we define it by

$$\epsilon/R^2 = \text{unit field}$$
$$= c\sqrt{(\lambda/2\kappa)}.$$

Using de Sitter's cosmology in which $\lambda = 3/R^2$, we get

$$2\kappa\epsilon^2/3c^2R = R.$$

Now, taking the mass of the electron as $2e^2/3c^2r$, where r is the electrical radius of the electron, we have

$$2\kappa\epsilon^2/3c^2r = \rho,$$

where ρ is the gravitational radius of the electron ; so that

$$\epsilon^2/e^2 = R^2/r\rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This shows that the "cosmic" unit of action ϵ^2/c (approximately the same as that calculated by Eddington in the references given above) and what we might call the "electronic" unit of action e^2/c are connected by the relative dimensions of the world and the electron. This suggests that the cosmic unit and the Planck quantum of action, h, may be connected in a similar fashion. The discovery of some fundamental connexion between the electronic unit of action and the quantum number is one of the problems of physical theory, and several interesting guesses at the nature of the pure number hc/e^2 have been offered. It may not be out of place to suggest that the cosmic unit and the Planck quantum may be related to one another through the size of the world and the size of some simple structure which enters into the make-up of "things." It seems obvious to propose the electron for the latter, but the numerical result obtained thereby is quite hopeless unless a value of the order 10^7 parsecs is chosen for R, which appears improbable. It occurs to the writer that since the quantum underlies in some mysterious way the dynamics of atomic phenomena, it may be plausible to assume that the structure referred to ought to contain an atomic dimension ; *e.g.*, the distance apart of nucleus and electron in the simplest combination of these two elements, viz., the normal hydrogen atom. Thus, taking this structure as a "tube" stretching from nucleus to electron, and writing a for the radius of the first Bohr circular orbit of the hydrogen atom, let us postulate that the cosmic unit of action and the Planck quantum have the same ratio as the volume of the world and the volume of this structure; *i.e.*,

$$\epsilon^2/hc = \pi^2R^3/\pi ar^2,$$

and so by (6)

$$e^2/hc = \pi R\rho/ar.$$

Now if m be the mass of the electron, we know by Bohr's theory that

$$a=h^2/4\pi^2me^2\,;$$

therefore

$$e^2/hc=4\pi^3R\rho me^2/h^2r$$

$$=(8\pi^3/3)(e^2/hc)^2.\,R\rho/r^2.$$

Hence

$$R\rho=(3hc/8\pi^3e^2)r^2. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

Relation (7) would fit in very well with the suggestion familiar to relativists (see Eddington's 'Space, Time, and Gravitation,' p. 179) that the electrical radius of the electron is of the same order of magnitude as the mean proportional between its gravitational radius and the radius of the world. It also gives a value of the order 10^{12} parsecs for R (2×10^{12}, however, instead of Silberstein's 5×10^{12}). Were it possible to write $8\pi^5/3$ for hc/e^2, the relation (7) would take quite an elegant form:

$$R\rho=\pi^2r^2.$$

Unfortunately the well-determined values for h and e seem to rule this out. At one time it appeared possible that π^6 might be equated to hc/e^2; but although $8\pi^5/3$ (approx. 816) is a better approximation than π^6 to the value of hc/e^2 (approx. 861, if $e=4{\cdot}78\times10^{-10}$; $h=6{\cdot}55\times10^{-27}$), it seems equally impossible. The preceding considerations, however, suggest that in some unknown way the important pure number hc/e^2 may be contained in the metrical relations of the structure of the world.

It may be of interest to point out that the energy-density of the unit field, *i. e.*, $\lambda/16\pi\kappa$ in *mass* units, is one-quarter of the density of the "world matter" required to fill the world on Einstein's own cosmology. Briefly, twice the natural field, if omnipresent, would on Einstein's views "swell out" the world to its proper size.

XLVIII. *The Critical Increment of Chemical Reactions.*

By WILLIAM EDWARD GARNER *.

IN the usual interpretation of the physical meaning of the constant A in the Arrhenius equation $d\log k/dT=A/RT^2$, it has been assumed that the experimental velocity constant k_1 corresponds to the velocity constant of the activations process. Thus, for a bimolecular reaction it is assumed that every collision between active molecules, or between molecules whose kinetic energies exceed a critical value, leads to chemical change. This conclusion would appear to be unsound, for there is no reason why a collision between active molecules should not give rise to reactants as well as to the resultants of the chemical reaction. If we assume the momentary formation of complexes between the reacting molecules, then the bimolecular reaction can be expressed by the following scheme :

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* Communicated by the Author.

$$A' + B' \underset{b}{\overset{a}{\rightleftharpoons}} \begin{matrix} AB' \\ \text{or} \\ CD' \end{matrix} \underset{d}{\overset{c}{\rightleftharpoons}} C' + D' + Q,$$

where reaction is assumed to occur between the activated molecules A' and B' and C' and D' respectively, to give the complex AB' or CD', which can then dissociate to give either the substances on the left or the right hand of the equation. There will be four distinct reactions, *a*, *b*, *c*, and *d*, and the corresponding velocity constants k_a, k_b, k_c, and k_d*. If k_1 is the measured velocity constant for the reaction $A+B \longrightarrow C+D$, it is clear that $k_1 = k_a \,.\, k_c/k_c+k_b$, where k_c/k_c+k_b is the fraction of the number of complexes which break down to give C and D.

Now the number of gram. mols. of complex formed from A and B per second $=k_a[A][B]$, and the number of molecules $=k_a N[A][B]$ where N is the Avogadro number, and if m and n represent the numbers of active molecules of A and B per gram. mol. and k is the number of collisions per litre per second between two molecules, then

$$k_a N[A][B] = kmn[A][B] ;$$

$$\therefore \quad k_1 = kmnk_c/N(k_c+k_b) :$$

and since k varies very slightly with temperature,

$$d \log mn/dT = -A/RT^2 - d \log (k_c/k_c+k_b)/dT.$$

The equilibrium between active and inactive molecules must be established very rapidly if the laws of mass action are to hold. Thus, in the equilibrium between A' molecules and A molecules, we shall have

$$d \log (m/N)/dT = -q_A/RT^2,$$

where q_A is the energy of activation for the change, $A \rightleftharpoons A'$; similarly

$$d \log (n/N)/dT = -q_B/RT^2.$$

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* k_a is the velocity constant for the reaction $A+B \longrightarrow AB'$, and k_d for the reaction $C+D \longrightarrow CD'$, expressed in gm. mols. per sec.

Thus

$$d \log mn/dT = -(q_A + q_B)/RT^2,$$

whence

$$(q_A + q_B)/RT^2 = A/RT^2 + d \log (k_c/k_c + k_b)/dT.$$

Thus $q_A + q_B = \Sigma h\nu$ the activation energy of the reactants may be greater or less than A the Arrhenius constant, according as the temperature coefficient of $k_c/k_c + k_b$ is negative or positive. The average energy of the complexes will increase with temperature; thus there is no *a priori* reason why $k_c/k_c + k_b$ should be independent of temperature. It follows that the critical increment is not necessarily the same as the activations energy, and that ν calculated therefrom may not coincide with the actual absorption bands of the reactants.

The Sir William Ramsay Inorganic and
Physical Chemistry Laboratories,
University College, London.
Dec. 7th, 1924.

XLIX. *Tides in a Channel.* *By* J. Proudman (*Tidal Institute, University of Liverpool*) *.

1. THE present investigation † relates to the tidal dynamics of a channel whose section is uniform along the length but of varying depth from side to side.

A short conjectural treatment of the problem was given by Sir G. B. Airy ('Tides and Waves,' §§ 358–363), but one of his results, viz. that "the ridge of wave cannot possibly stretch transversely to the channel," is erroneous, as will be seen below (§ 2). Another of his results, viz. a rule for the direction of rotation of tidal currents, is valid, however, over wider conditions than Airy considered (§ 3).

After making general deductions concerning a section of any shape, attention is concentrated on a parabolic section (§ 4). One result is to show the degree of accuracy involved in the approximations of what may be called the "narrow sea theory." This is the theory which in recent years has been shown, notably by R. Sterneck and A. Defant, to account for many of the observed features of tides in gulfs, channels, and narrow seas.

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* Communicated by the Author.

† Part of the Adams Prize Essay, 1923. The author is much indebted to Dr. A. T. Doodson for the calculations involved in the illustrations.

The essential characteristic of the narrow sea theory is that transverse currents are neglected, so that the motion is assumed to consist of longitudinal oscillations whose currents maintain oscillating transverse gradients in virtue of the Earth's rotation. By introducing geometrical simplicity into the basin it is possible to take account of the transverse currents and then to compare the results with those obtained on neglecting these currents. We find that if the channel is not too wide or too shallow the degree of accuracy of the narrow sea theory is high, but that this degree of accuracy decreases as the effect of the Earth's rotation becomes important.

2. *General Equations.*

We shall denote by

ω the component of the Earth's angular velocity along the vertical at the latitude of the channel,

g the acceleration due to gravity,

x, y Cartesian coordinates of position in the longitudinal and transverse directions respectively,

a_1, a_2 the values of y along the sides of the channel, so that the breadth of the channel is a_2-a_1,

h the depth of water below any point of the mean surface,

A the area of a vertical transverse section of the channel,

t the time,

ζ the elevation of the free surface of the water at any time above any point on the mean surface,

$\bar{\zeta}$ the mean elevation at any time along the surface-line of any transverse section,

u, v the longitudinal and transverse components of current at any point and time,

$\bar{u}$ the mean value of the longitudinal component of current over any vertical transverse section at any time.

We shall suppose that the motion is "small" and retain only terms of the first order.

The equation of continuity takes the form

$$\frac{\partial}{\partial x}(hu)+\frac{\partial}{\partial y}(hv)+\frac{\partial \zeta}{\partial t}=0, \quad . \quad . \quad . \quad (2.11)$$

while at the sides of the channel we have

$$hv \rightarrow 0, \quad \text{as} \quad y \rightarrow a_1, a_2. \quad . \quad . \quad . \quad (2.12)$$

In the absence of astronomical and frictional forces the equations of motion take the form

$$\frac{\partial u}{\partial t} - 2\omega v = -g\frac{\partial \zeta}{\partial x}, \qquad \frac{\partial v}{\partial t} + 2\omega u = -g\frac{\partial \zeta}{\partial y}. \quad (2.13)$$

Now suppose that

$$\left.\begin{aligned} \zeta &= \mathrm{Z}\cos(\sigma t - \kappa x), \\ u &= \mathrm{U}\cos(\sigma t - \kappa x), \\ v &= \mathrm{V}\sin(\sigma t - \kappa x), \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (2.21)$$

where σ and κ are constants, and Z, U, V are functions only of y. We regard σ as prescribed so that the values of κ will be determined by the basin. On substituting from (2.21) into (2.11) and (2.13), we obtain

$$\kappa h\mathrm{U} + \frac{d}{dy}(h\mathrm{V}) - \sigma\mathrm{Z} = 0, \quad . \quad . \quad . \quad (2.22)$$

$$\sigma\mathrm{U} + 2\omega\mathrm{V} = \kappa g\mathrm{Z}, \qquad \sigma\mathrm{V} + 2\omega\mathrm{U} = -g\frac{d\mathrm{Z}}{dy}, \quad (2.23)$$

and then deduce

$$\frac{d}{dy}(h\mathrm{V}) - \frac{2\omega}{\sigma}\kappa h\mathrm{V} = \frac{\kappa^2}{\sigma}\left(\frac{\sigma^2}{\kappa^2} - gh\right)\mathrm{Z}. \quad . \quad (2.24)$$

From (2.24) and the boundary condition at $y = a_1$ we deduce

$$h\mathrm{V} = \frac{\kappa^2}{\sigma}e^{\frac{2\omega}{\sigma}\kappa y}\int_{a_1}^{y}\left(\frac{\sigma^2}{\kappa^2} - gh\right)\mathrm{Z}e^{-\frac{2\omega}{\sigma}\kappa y}\,dy, \quad . \quad (2.25)$$

so that the boundary condition at $y = a_2$ gives

$$\int_{a_1}^{a_2}\left(\frac{\sigma^2}{\kappa^2} - gh\right)\mathrm{Z}e^{-\frac{2\omega}{\sigma}\kappa y}\,dy = 0. \quad . \quad . \quad (2.26)$$

On solving equations (2.23) we have, providing $\sigma \neq \pm 2\omega$,

$$\frac{\sigma^2 - 4\omega^2}{\sigma g}\mathrm{U} = \kappa\mathrm{Z} + \frac{2\omega}{\sigma}\frac{d\mathrm{Z}}{dy}, \qquad \frac{\sigma^2 - 4\omega^2}{\sigma g}\mathrm{V} = -\frac{d\mathrm{Z}}{dy} - \frac{2\omega}{\sigma}\kappa\mathrm{Z}, \quad . \quad . \quad . \quad (2.27)$$

and then on substituting into (2.22) we have

$$\frac{d}{dy}\left(h\frac{d\mathrm{Z}}{dy}\right) + \left(\frac{\sigma^2 - 4\omega^2}{g} - \kappa^2 h + \frac{2\omega}{\sigma}\kappa\frac{dh}{dy}\right)\mathrm{Z} = 0. \quad (2.28)$$

The condition to be satisfied at the sides may be written as

$$h\left(\frac{d\mathrm{Z}}{dy} + \frac{2\omega}{\sigma}\kappa\mathrm{Z}\right) \rightarrow 0, \qquad y \rightarrow a_1, a_2. \quad . \quad . \quad (2.29)$$

2 H 2

The special cases $\sigma=\pm 2\omega$ require separate treatment. We take $\sigma=2\omega$, which corresponds to a semi-diurnal tide at the North Pole or to a diurnal tide in north latitude 30°.

The equations (2.23) take the form

$$\frac{\sigma}{g}(\mathrm{U}+\mathrm{V})=\kappa\mathrm{Z}=-\frac{d\mathrm{Z}}{dy}, \quad . \quad . \quad . \quad (2.31)$$

so that

$$\kappa\mathrm{Z}=e^{-\kappa y}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.32)$$

on dropping a constant numerical factor. Equation (2.26) then becomes

$$\int_{a_1}^{a_2}\left(\frac{\sigma^2}{\kappa^2}-gh\right)e^{-2\kappa y}\,dy=0, \quad . \quad . \quad . \quad (2.33)$$

and we notice that there is only one real value of κ.

In the "narrow sea theory" equation (2.11) is replaced by

$$\frac{\partial}{\partial x}(\mathrm{A}\bar{u})+(a_2-a_1)\frac{\partial\bar{\zeta}}{\partial t}=0, \quad . \quad . \quad . \quad (2.41)$$

while equations (2.13) are replaced by

$$\frac{\partial u}{\partial t}=-g\frac{\partial\bar{\zeta}}{\partial x}, \qquad 2\omega\bar{u}=-g\frac{\partial\zeta}{\partial y}, \quad . \quad . \quad (2.42)$$

though of course in applications A and a_2-a_1 are functions of x. Then (2.22) becomes replaced by

$$\kappa\bar{\mathrm{U}}-\sigma/\bar{h}\,.\,\bar{\mathrm{Z}}=0, \quad . \quad . \quad . \quad . \quad (2.43)$$

where

$$\bar{h}=\mathrm{A}/(a_2-a_1)=\int_{a_1}^{a_2}h\,dy\Big/\int_{a_1}^{a_2}dy, \quad . \quad . \quad (2.44)$$

while (2.23) becomes replaced by

$$\sigma\bar{\mathrm{U}}=\kappa g\bar{\mathrm{Z}}, \qquad 2\omega\bar{\mathrm{U}}=-g\frac{d\mathrm{Z}}{dy}, \quad . \quad . \quad (2.45)$$

where $\bar{\mathrm{Z}}$, $\bar{\mathrm{U}}$ are mean values of Z, U across any transverse section at any time. We deduce that

$$\kappa^2=\sigma^2/g\bar{h}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.46)$$

3. *Transverse Current.*

In this section we restrict our consideration to cases in which Z remains positive across the channel.

Equation (2.26) may be written in the form

$$\sigma^2/\kappa^2=gh_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.11)$$

where

$$h_1 = \int_{a_1}^{a_2} hZe^{-\frac{2\omega}{\sigma}\kappa y}\,dy \Big/ \int_{a_1}^{a_2} Ze^{-\frac{2\omega}{\sigma}\kappa y}\,dy. \quad . \quad (3.12)$$

We deduce that the value of h_1 will lie between the greatest and least values of h.

Equation (2.25) shows that if there is a shelving beach at $y=a_1$ there will be a neighbouring region over which V is positive, while (2.25) and (2.26) together show that if there is a shelving beach at $y=a_2$ there will be a neighbouring region over which V is negative. We deduce that if there is a shelving beach on either side of the channel, there will be a neighbouring region over which at a quarter period before high water the current is directed towards the shore. This is *Airy's Rule* (*l. c.* § 362), though his argument seems to depend on his erroneous result and he took no account of the Earth's rotation.

If there is a shelving beach at both sides of the channel, there must be at least two values of y for which $h=h_1$. The simplest natural case arises when there are only two such values of y, say y_1, y_2. In this case

$$hVe^{-\frac{2\omega}{\sigma}\kappa y}$$

will increase from zero at $y=a_1$ to a maximum at $y=y_1$, then decrease to a minimum at $y=y_2$, and finally increase to zero at $y=a_2$. It follows that for a certain value of y, say y_0, between y_1 and y_2, V will change sign and that for $a_1<y<y_0$, V will be positive, while for $y_0<y<a_2$, V will be negative (*cf.* fig. 1). On either side of $y=y_0$ along any section the transverse current at any time preserves the same sign and this sign changes at $y=y_0$. A quarter period before high water the current is directed towards the corresponding shore.

4. *Parabolic Section.*

We now restrict our consideration to the parabolic section given by

$$h = h_0(1-y^2/a^2), \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

h_0 and a being constants, so that $a_1=-a$, $a_2=a$.

We deduce

$$\bar{h} = \tfrac{2}{3}h_0,$$

so that the *narrow sea theory* gives

$$\kappa^2 = \tfrac{3}{2}\sigma^2/gh_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.2)$$

by (2.46).

Taking now the *special case* $\sigma=2\omega$, we deduce from (2.33)

$$\frac{\tanh 2\kappa a}{2\kappa a}=\frac{1}{1+2\sigma^2a^2/gh_0}. \quad . \quad . \quad . \quad (4.31)$$

If $a=100$ km., $h_0=100$ m., $\sigma=\cdot 00014$ rad./sec. (semi-diurnal tides), we find $\sigma^2a^2/gh_0=0\cdot 2$.

The second column of the Table shows the ratio of κ^2 as given by (4.31) to its value as given by the narrow sea theory.

$\dfrac{\sigma^2a^2}{gh_0}$.	$\kappa^2\Big/\dfrac{3}{2}\dfrac{\sigma^2}{gh_0}$.	$1+\dfrac{2}{5}\dfrac{\sigma^2a^2}{gh_0}$.
·1	1·04	1·04
·2	1·09	1·08
·3	1·13	1·12
·4	1·18	1·16
·5	1·22	1·20
·6	1·27	1·24
·7	1·32	1·28
·8	1·38	1·32
·9	1·43	1·36
1·0	1·49	1·40

For small values of σ^2a^2/gh_0 we have, to the second order,

$$\kappa^2=\frac{3}{2}\frac{\sigma^2}{gh_0}\left(1+\frac{2}{5}\frac{\sigma^2a^2}{gh_0}\right). \quad . \quad . \quad . \quad (4\cdot 311)$$

The third column of the Table shows the ratio of the value of κ^2 as given by (4.311) to that given by the narrow sea theory.

From (2.25) and (2.32) we deduce

$$\begin{aligned}\frac{\sigma}{gh_0}hV&=\frac{1}{2}\frac{e^{\kappa a}}{\kappa^2a^2}\left[\left\{1+\frac{2\sigma^2a^2}{gh_0}-\kappa^2(a^2-y^2)-\kappa(a-y)\right\}\sinh\kappa(a+y)\right.\\&\qquad\left.+\{\kappa^2(a^2-y^2)-\kappa(a+y)\}\cosh\kappa(a+y)\right]. \quad . \quad (4.32)\end{aligned}$$

From (2.31) and (2.32) we have

$$\begin{aligned}\frac{\sigma}{gh_0}hU&=\frac{1}{2}\frac{e^{\kappa a}}{\kappa^2a^2}\left[\left\{1+\frac{2\sigma^2a^2}{gh_0}+\kappa^2(a^2-y^2)-\kappa(a-y)\right\}\sinh\kappa(a+y)\right.\\&\qquad\left.-\{\kappa^2(a^2-y^2)+\kappa(a+y)\}\cosh\kappa(a+y)\right]. \quad . \quad (4.33)\end{aligned}$$

Figs. 1 and 2 show respectively the graphs of (4.32) and (4.33) from $y=-a$ to $y=a$, for $\sigma^2a^2/gh_0=0\cdot1$, $0\cdot5$, $1\cdot0$.

We notice that the line along which the transverse currents vanish is nearer to the left of the channel, looking in the direction of propagation of the wave, and that this lack of symmetry increases with the value of σ^2a^2/gh_0. When

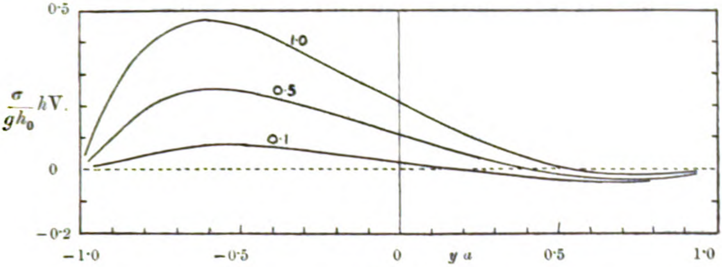

Fig. 1.

Showing distribution of transverse current across breadth of channel, looking in direction opposite to that of propagation of wave. Figures on curves are corresponding values of σ^2a^2/gh_0.

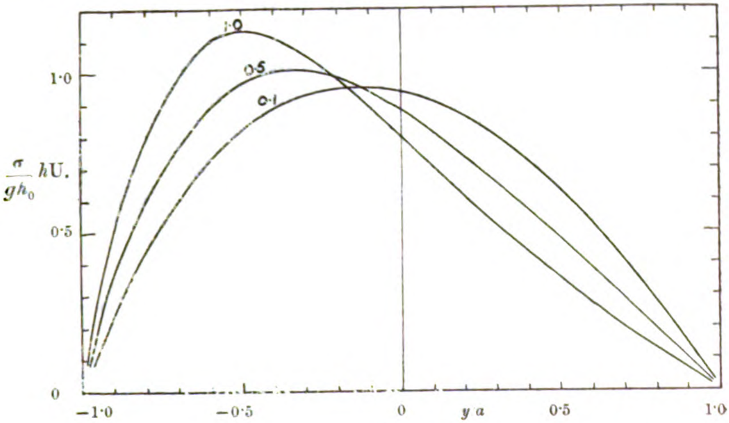

Fig. 2.

Showing distribution of longitudinal current across breadth of channel, looking in direction opposite to that of propagation of wave. Figures on curves are corresponding values of σ^2a^2/gh_0.

$\sigma^2a^2/gh_0=1$ the breadth of the left-hand region is relatively small and its currents are also relatively small. The ratio of transverse to longitudinal current reaches a maximum at the right side of the channel; its values for the cases of $\sigma^2a^2/gh_0=0\cdot1$, $0\cdot5$, $1\cdot0$ are $0\cdot15$, $0\cdot35$, $0\cdot51$ respectively.

Next let us suppose that the channel is *non-rotating* so that $\omega=0$, as would occur at the Equator.

On substituting into (2.28) from (4.1) we have

$$\frac{d}{dy}\left\{\left(1-\frac{y^2}{a^2}\right)\frac{dZ}{dy}\right\}+\left\{\frac{\sigma^2}{gh_0}-\kappa^2\left(1-\frac{y^2}{a^2}\right)\right\}Z=0. \quad (4.41)$$

For the symmetrical solution we assume the infinite series

$$Z=A_0+A_2\frac{y^2}{a^2}+\,..\,+A_n\frac{y^n}{a^n}+\ldots, \quad . \quad (4.42)$$

where n is even, and on substituting we obtain

$$2A_2+\left(\frac{\sigma^2a^2}{gh_0}-\kappa^2a^2\right)A_0=0, \quad . \quad . \quad . \quad (4.43)$$

and

$$(n+2)(n+1)A_{n+2}-(n+1)nA_n$$
$$+(\sigma^2a^2/gh_0-\kappa^2a^2)A_n+\kappa^2a^2A_{n-2}=0. \quad . \quad (4.44)$$

From (2.29) we require a value of κ which will make

$$\left(1-\frac{y^2}{a^2}\right)\frac{dZ}{dy}\rightarrow 0,$$

as $y\rightarrow a$, and to find this we may use the celebrated argument initiated by Laplace for an ocean covering the whole globe. We have from (4.44)

$$\frac{A_{n+2}}{A_n}=\frac{n}{n+2}+\frac{\kappa^2a^2-\sigma^2a^2/gh_0}{(n+2)(n+1)}-\frac{\kappa^2a^2}{(n+2)(n+1)}\bigg/\frac{A_n}{A_{n-2}},$$
$$. \quad . \quad . \quad (4.441)$$

so that A_{n+2}/A_n tends either to 1 or 0 as $n\rightarrow\infty$.

In the former case we have, as the principal part,

$$\frac{A_{n+2}}{A_n}=\frac{n}{n+2},$$

so that the series (4.42) behaves like

$$\frac{1}{2}\frac{y^2}{a^2}+\frac{1}{4}\frac{y^4}{a^4}+\ldots+\frac{1}{n}\frac{y^n}{a^n}+\ldots$$

or

$$-\tfrac{1}{2}\log\left(1-\frac{y^2}{a^2}\right),$$

which is inadmissible as an expression for Z.

We therefore require those values of κ which make

$$\frac{A_{n+2}}{A_n}\rightarrow 0, \text{ as } n\rightarrow\infty, \quad . \quad . \quad . \quad . \quad (4.45)$$

On writing

$$\alpha_n = \frac{n}{n+2} + \frac{\kappa^2 a^2 - \sigma^2 a^2/gh_0}{(n+2)(n+1)}, \qquad \beta_n = \frac{\kappa^2 a^2}{(n+2)(n+1)}, \qquad (4.46)$$

we have

$$\frac{A_n}{A_{n-2}} = \frac{\beta_n}{\alpha_n - A_{n+2}/A_n},$$

so that

$$\frac{A_2}{A_0} = \frac{\beta_2}{\alpha_2 -}\,\frac{\beta_4}{\alpha_4 -}\cdots\frac{\beta_n}{\alpha_n -}\cdots$$

on the assumption (4.45). But $A_2/A_0 = \alpha_0$, so that

$$\alpha_0 - \frac{\beta_2}{\alpha_2 -}\,\frac{\beta_4}{\alpha_4 -}\cdots\frac{\beta_n}{\alpha_n -}\cdots = 0, \quad . \quad . \quad (4.47)$$

n being even, and this is the equation for the possible values of κ.

With $\sigma^2 a^2/gh_0$ small, we have as a first approximation to the lowest real root of (4.47)

$$\kappa^2 = \tfrac{3}{2}\sigma^2/gh_0, \quad . \quad . \quad . \quad . \quad . \quad (4.471)$$

as in the narrow sea theory. As the next approximation to the lowest real root, we have

$$\kappa^2 = \frac{3}{2}\frac{\sigma^2}{gh_0}\left(1 + \frac{1}{30}\frac{\sigma^2 a^2}{gh_0}\right), \quad . \quad . \quad . \quad (4.472)$$

which shows that the first approximation is very good.

Let us finally take the case of a *general rotation*. Equation (2.28) with (4.1) gives*

$$a^2\frac{d}{dy}\left\{\left(1-\frac{y^2}{a^2}\right)\frac{dZ}{dy}\right\}$$

$$+\left\{\frac{\sigma^2 a^2 - 4\omega^2 a^2}{gh_0} - \kappa^2(a^2-y^2) - \frac{4\omega}{\sigma}\kappa y\right\}Z = 0. \quad (4.51)$$

Into this equation let us substitute the finite series

$$Z = A_0 + A_1\frac{y}{a} + A_2\frac{y^2}{a^2} + \ldots + A_n\frac{y^n}{a^n} + \ldots + A_m\frac{y^m}{a^m}. \quad (4.52)$$

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* The author has learnt that Dr. G. R. Goldsbrough examined this problem some years ago.

Then the left-hand side becomes

$$\begin{aligned}
&\left[\left(\frac{\sigma^2a^2-4\omega^2a^2}{gh_0}-\kappa^2a^2\right)A_0+2\,.\,1\,.\,A_2\right]\\
&+\Bigg[-\frac{4\omega}{\sigma}\kappa a\,A_0\\
&\qquad+\left\{\frac{\sigma^2a^2-4\omega^2a^2}{gh_0}-\kappa^2a^2-2\,.\,1\right\}A_1+3\,.\,2\,.\,A_3\Bigg]\frac{y}{a}\\
&\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad,\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\\
&+\Bigg[\kappa^2a^2A_{n-2}-\frac{4\omega}{\sigma}\kappa a\,A_{n-1}\\
&\qquad+\left\{\frac{\sigma^2a^2-4\omega^2a^2}{gh_0}-\kappa^2a^2-(n+1)n\right\}A_n\\
&\qquad+(n+2)(n+1)\,A_{n+2}\Bigg]\frac{y^n}{a^n}\\
&\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\\
&+\Bigg[\kappa^2a^2A_{m-3}-\frac{4\omega}{\sigma}\kappa a\,A_{m-2}\\
&\qquad+\left\{\frac{\sigma^2a^2-4\omega^2a^2}{gh_0}-\kappa^2a^2-m(m-1)\right\}A_{m-1}\Bigg]\frac{y^{m-1}}{a^{m-1}}\\
&+\Bigg[\kappa^2a^2A_{m-2}-\frac{4\omega}{\sigma}\kappa a\,A_{m-1}\\
&\qquad+\left\{\frac{\sigma^2a^2-4\omega^2a^2}{gh_0}-\kappa^2a^2-(m+1)m\right\}A_m\Bigg]\frac{y^m}{a^m}\\
&+\left[\kappa^2a^2A_{m-1}-\frac{4\omega}{\sigma}\kappa a\,A_m\right]\frac{y^{m+1}}{a^{m+1}}\\
&+\left[\kappa^2a^2A_m\right]\frac{y^{m+2}}{a^{m+2}}.\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad(4.53)
\end{aligned}$$

Now by proper choice of the m ratios

$$A_0:A_1:\ldots\ldots:A_{m-1}:A_m,$$

we can make zero the coefficients of y^n/a^n for

$$n=0,1,\ldots\ldots,m-1,$$

and by special choice of κ we can make zero the coefficient of y^m/a^m. We then see that (4.52) is a solution of (4.51) modified by the addition of

$$\left\{ \kappa^2 a^2 A_{m-1} - \frac{4\omega}{\sigma} \kappa a \, A_m \right\} \frac{y^{m+1}}{a^{m+1}} + \kappa^2 a^2 A_m \frac{y^{m+2}}{a^{m+2}} \quad (4.54)$$

to the right-hand side, and that the boundary conditions,

$$\left(1 - \frac{y^2}{a^2}\right)\left(\frac{dZ}{dy} + \frac{2\omega}{\sigma} \kappa Z\right) \to 0,$$

as $y \to \pm a$, are also satisfied.

Now the vanishing of the coefficient of y^n/a^n shows that after n reaches a certain value $| A_{n+2} |$ is less than the greatest of

$$| A_{n-2} | , \; | A_{n-1} | , \; | A_n |,$$

and then the vanishing of the coefficients of y^{m-1}/a^{m-1} and y^m/a^m shows that as $m \to \infty$

$$A_{m-1}, \quad A_m \to 0.$$

We therefore see that, by taking m large enough, we can, with the choice of κ we have indicated, make (4.52) as near a solution of (4.51) as we please.

The equation for the possible values of κ is

$$\begin{vmatrix} \left(\kappa^2 - \dfrac{\sigma^2 - 4\omega^2}{gh_0}\right) a^2, & 0 \quad , & -2 & , \dots \\ \dfrac{1}{2 \, . \, 1} \dfrac{4\omega}{\sigma} \kappa a & , \; 1 + \dfrac{1}{2 \, . \, 1} \left(\kappa^2 - \dfrac{\sigma^2 - 4\omega^2}{gh_0}\right) a^2, & 0 & , \dots \\ -\dfrac{1}{3 \, . \, 2} \kappa^2 a^2 \quad , & \dfrac{1}{3 \, . \, 2} \dfrac{4\omega}{\sigma} \kappa a & , \; 1 + \dfrac{1}{3 \, . \, 2} \left(\kappa^2 - \dfrac{\sigma^2 - 4\omega^2}{gh_0}\right) a^2, & \dots \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix} = 0. \quad . \quad . \quad . \quad (4.55)$$

If σ and ω are of the same order and $\sigma^2 a^2 / gh_0$ may be regarded as small, we have, to the second order,

$$\kappa^2 = \frac{3}{2} \frac{\sigma^2}{gh_0} \left\{ 1 + \frac{\sigma^2 + 44\omega^2}{30 gh_0} a^2 \right\}, \quad . \quad . \quad . \quad (4.551)$$

which includes (4.311) and (4.472) as particular cases.

L. *A Modification of Rankine's Theory of Earth Pressures on Retaining Walls.* *By* WILLIAM J. WALKER, *Ph.D.*, *University College, Dundee* *.

OF the two principal theories of earth pressure, Rankine's and Coulomb's, the general tendency in favour of the latter is strikingly exemplified by the many "wedge" theories, all modifications of Coulomb's, which have been introduced by various authorities. This has been largely due to the generally excessive values obtained, by calculation from Rankine's formula, for the pressure on a vertical wall,

$$P=\tfrac{1}{2}wh^2\cos\theta\left\{\frac{\cos\theta-\sqrt{\cos^2\theta-\cos^2\phi}}{\cos\theta+\sqrt{\cos^2\theta-\cos^2\phi}}\right\}$$

$$=\tfrac{1}{2}wh^2K, \qquad \ldots \qquad (1)$$

where θ is the angle of surcharge
and ϕ is the angle of repose,

the direction of P being parallel to the surface slope.

On the other hand, the application of the somewhat cumbersome Coulomb formula,

$$P=\tfrac{1}{2}wh^2\frac{\sin^2(\delta-\phi)}{\sin^2\delta\sin^2(\delta+z)\left\{1+\sqrt{\dfrac{\sin(z+\phi)\sin(\phi-\theta)}{\sin(\delta+z)\sin(\delta-\theta)}}\right\}}$$

[where θ and ϕ are as before, δ is angle which wall makes with vertical, and z is angle which resultant P makes with wall], or one of its many modifications, gives, in general, pressures which are more in agreement with results relating to the particular problem which may be under review. For a non-vertical wall, of course, Rankine's formula requires the addition or subtraction of the thrust due to the weight of the triangular prism of earth between the vertical and either the face or back of the wall according to the direction of inclination.

There is no doubt, however, that the existence of so many "wedge" theories, derived from the parent theory of Coulomb, indicates a lack of generality in the method. In particular cases, this or that wedge theory may be capable of giving closely approximate results to actual practical values, but none of them alone appear comprehensive enough to cover the wide diversity of earth-pressure problems which may require solution. To the writer's mind, the main objection to the wedge type of theory, apart from the fictitious "plane of cleavage" which it postulates, is the implicit neglect of the extent of the supporting mass of earth beyond the wedge.

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* Communicated by the Author.

Rankine's theory follows more orthodox and fundamental lines, and it is more than probable that the lack of sufficient experimental data is all that prevented him from introducing the necessary correctives to his preliminary assumptions. In the derivation of his formula he assumed that the granular earth material

(*a*) possessed an indefinitely extended upper surface,

and

(*b*) was incompressible.

Superficially, these two assumptions appear to be valid enough to give a formula capable of fairly general application. The modification which, in the light of all the data available, appears to be required in his theory lies in the abolition of the assumption of an infinitely extended surface. The writer here proposes to introduce this modification to Rankine's theory, and then to show, by application to specific tests, that the modified theory is capable of general application, besides possessing a more rational foundation than any wedge theory.

Two of the consequences of Rankine's assumption of an infinitely extended surface are that the vertical pressure and its conjugate for the granular material must vary directly as the depth, and that the centre of pressure on any plane rectangular surface, partially immersed in the material, must lie at two-thirds the depth of the plane from the surface of the material. These two results are at variance with all experience of earth pressures.

Taking, then, as the point of departure from Rankine's theory the assumption of a finitely extended surface, assume that sand or other granular material is contained in a cylinder of any peripheral form with vertical walls. The pressure p, at any depth, taken parallel to the surface slope, is given, in terms of the vertical pressure, q by

$$p=q\mathrm{K},$$

where K denotes the same expression as it does in (1).

Considering now the equilibrium of a cross-sectional element of the cylinder of thickness dx in the vertical direction, the section being taken parallel to the surface slope, the upward force of friction supporting the element is given by

$$F = L_1\,dx\,p\tan\phi\cos\theta,$$

where L_1 is the periphery of the element, and the assumption is made that the friction between the wall and the granular material is the same as the internal friction of the material. Evidently, therefore, the upward intensity of pressure over the cylindrical cross-section of the element, due to this friction on the walls, may be written

$$\frac{F}{A} = \frac{L\,dx\,p\tan\phi}{A} = kq\,dx, \quad . \quad . \quad . \quad . \quad (2)$$

where L and A are the periphery and cross-sectional area respectively of the cylinder for a horizontal section, and k is a constant depending on the geometrical form of the cylinder, the angle of repose ϕ, and the angle of surcharge θ, and is given by

$$k = \frac{KL\tan\phi}{A}.$$

The equation of equilibrium of the element may therefore be written

$$dq = w\,dx - kq\,dx, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where w is the specific weight of the granular material. If the cylindrical mass carries a load W on its surface, the solution of (3) gives, for the pressure intensity q at any depth h, the equation

$$q = \frac{w}{k}\left\{1 - e^{-kh}\left(1 - \frac{kW}{wA}\right)\right\}.$$

Writing

$$c = 1 - \frac{kW}{wA},$$

the resultant pressure P on unit width of wall is given by

$$P = \frac{wK}{k}\int_0^h (1 - ce^{-kh})\,dh$$

$$= \frac{wA}{L\tan\phi}\left\{h + \frac{c}{k}(e^{-kh} - 1)\right\}, \quad . \quad . \quad (4)$$

and is parallel to the surface slope.

The foregoing analysis has been developed in all its generality without specifying any particular form of boundary wall. In practice, however, these invariably form plane surfaces, and attention will now be confined to these. It should be observed that, although in general there may not be boundary wall on all sides of the mass of granular material, nevertheless at such points where no boundary wall exists the material will take up its natural angle of repose, and the assumption of a vertical boundary wall through the top edge of the natural bank thus formed fulfils the statical conditions of the problem.

Since the overturning moment on a wall is just as important a factor in design as the resultant pressure, it is necessary to determine the centre of pressure of the wall—*i.e.*, the point at which the resultant pressure acts. The equation to determine the depth H of the centre of pressure of a plane vertical wall is given by

$$H\Sigma p\,ds = \Sigma hp\,ds,$$

where *ds* is the small surface element at which p acts.

But

$$p = \frac{wK}{k}(1 - ce^{-kh}).$$

∴ For a vertical line element of wall

$$H[\Sigma\, dh - c\Sigma e^{-kh}\, dh] = [\Sigma h\, dh - c\Sigma he^{-kh}\, dh].$$

$$\therefore\quad H\left[\int_0^h dh - c\int_0^h e^{-kh}\, dh\right] = \left[\int_0^h h\, dh - c\int_0^h he^{-kh}\, dh\right],$$

which gives

$$H = \frac{\frac{h^2}{2} + \frac{c}{k^2}[\{e^{-kh}(kh+1) - 1\}]}{h + \frac{c}{k}(e^{-kh} - 1)},$$

where h is the covered depth of the wall.

Expressions (4) and (5), therefore, are the modified formulæ for obtaining the resultant pressure, the centre of pressure, and therefore the overturning moment on a retaining wall. Applying these to experiments carried out by Prof. A. R. Fulton[*], the following table has been drawn up, the experimental results in which correspond to Table I. of Prof. Fulton's paper. The values of K and *k* were calculated from the given data.

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[*] "Overturning Moment on Retaining Walls," Proc. I. C. E. ccix. part i. (1919-20).

		No surcharge—Wall vertical.								
	Material.	Gravel.			Sand.			Earth.		
	h feet	3	5	7	3	5	7	3	5	7
	Experimental moment—lb. feet	91	480	1092	78	364	936	60	300	728
Calculated moments.	Wedge formula	93	431	1182	75	345	948	57	262	719
	Rankine's ,,	122	560	1537	99	457	1255	77	355	973
	Modified ,,	97	462	1170	84	378	942	65	300	758

It will be observed that the calculated values obtained from the modified formula give a maximum excess of calculated pressure of about 8 per cent. and a maximum deficit of 5 per cent., whereas the wedge formula gives corresponding maxima of excess and deficit of 8 and 12 per cent. respectively.

From the foregoing, therefore, it is clear that Rankine's theory of earth pressures, fundamental as it is in character, is perfectly capable, when modified in the manner indicated, of giving results closely approximate to those to be expected in practice.

LI. *On an Application of the Periodogram to Wireless Telegraphy.*

By C. R. BURCH, *B.A.*, *and* J. BLOEMSMA, *M.N.I.R.E.**

SUMMARY.

THIS paper discusses the response of a wireless receiver to morse signals and also to atmospherics, in terms of the periodogram of the pulse, and the resonance curve of the receiver. The effect of heterodyne detection is examined, and the shape of the resonance curve of the ideal receiver is discussed.

The relative merits of open and closed antennæ are determined, and a weakness of the limiter selector-method of reception is indicated.

I. INTRODUCTION.

IT is often said that a non-periodic oscillation "contains all frequencies." It is the object of this paper to assign a definite quantitative interpretation to this statement, and to draw therefrom certain conclusions as to the behaviour of resonant systems under impulse excitation.

* Communicated by Dr. W. H. Eccles, F.R.S.

For a fuller mathematical treatment of the same subject, of very rigid nature, reference should be made to the work of Dr. A. Koerts, 'Atmosphärische Storungen in der drahtlosen Nachrichtenubermittlung,' to which the attention of the authors has been drawn since the completion of this paper, which is now offered in view of its different extension into detail, and its simpler attack.

Let the non-periodic oscillation be given by $E=f(t)$ from $t=0$ to $t=\infty$, where the function f, finite and single-valued for all values of t, and vanishing at $t=\infty$, is restricted to a type expandible as a Fourier series.

An example of sufficient conditions is as follows:—

The function f should have only a finite number of maxima, minima, and discontinuities in any finite range of t, and it should vanish at $t=\infty$ to a higher order than t^{-1}.

The Periodogram of E, $=f(t)$, a complex function, $X_q, = (a_q+ib_q)$ of $f(t)$ and the parameter q, defined as

$$X_q = \int_0^\infty f(t) \, . \, \epsilon^{iqt} \, . \, dt,$$

where ϵ is the base of natural logarithms and $i \equiv \sqrt{-1}$, will then exist as the limit of a sum.

$X_q dq$ represents in magnitude and phase π times the contribution to E arising from pulsatances q to $q+dq$, for E may be written as the real part of

$$\frac{1}{\pi}\int_0^\infty X_q \epsilon^{-iqt} = dq. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$|X_q|^2 . dq, = (a_q{}^2 + b_q{}^2)$, is π times the contribution to $\int_0^\infty E^2 dt$ due to pulsatances q to $q+dq$, and

$$\int_0^\infty E^2 dt = \frac{1}{\pi}\int_0^\infty |X_q|^2 . dq. \quad . \quad . \quad . \quad . \quad (2)$$

The validity of (1) and (2) follows from the fact that they are the limiting forms of the Fourier treatment of the function f, over a finite time, as that time is made indefinitely great.

The definition of X_q determines it uniquely in terms of $f(t)$, and it follows from (2) that the periodogram determines the function uniquely, for if two different functions had the same periodogram, a difference-function would exist having X_q zero for all values of q.

It would then have $\int_0^\infty E^2 dt$ zero, and therefore E zero for all time. In fact, the two supposedly different functions are identical.

The subject has been treated by Lord Rayleigh, "Remarks concerning Fourier's Theorem as applied to Physical Problems," Phil. Mag. xxiv. pp. 864–869 (1912). It is there shown that smoothing the function f annuls X_q for large values of q, while smoothing X_q as a function of q annuls the equivalent function, f, for values of t numerically great.

In wireless problems E may represent any electrical quantity (electric force, current, charge). In using the periodogram to deduce from the form of $f(t)$ the behaviour of any of these quantities (Q) in a resonant system, it is necessary to consider also a similar complex function, $Y_{q,(Q,E)}, = x_q + iy_q$, a function of the circuit constants and the parameter q.

We contemplate only systems having for every possible free vibration a finite, positive, damping exponent. For such systems, $Y_q(Q, E)$ is so defined that if E were periodic, and equal to the real part of $E_0\epsilon^{iqt}$, Q in the branch under examination (not necessarily that in which E is present) would, after infinite time, be the real part of $Y_qE_0\epsilon^{iqt}$.

Thus in a simple LRC circuit, if E is the induced voltage, and we wish to examine the current (Q), we write

$$Y_q = \frac{iqC}{1-q^2LC+iqCR}.$$

In the case of $E=f(t)$, (Q) may be written as the real part of

$$\frac{1}{\pi}\int_0^{\infty} \epsilon^{-iqt} X_q \,.\, Y_q \,.\, dq. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This form is intractable analytically, and is unsuitable for numerical calculation in the case when the mathematical expressions represent only approximately the exact physical conditions—a difficulty met with in many of the formulæ of mathematical physics.

Though it may be present to such an extent as to render integral (3) as it stands, devoid of meaning, the less general form

$$\int_0^{\infty} Q^2 dt = \frac{1}{\pi}\int_0^{\infty} |X_q|^2 \,.\, |Y_q|^2 \,.\, dq \quad . \quad . \quad . \quad (4)$$

will still afford a basis for numerical computation.

The validity of (3) and (4) follows in the same way as that of (1) and (2), for they are the limiting forms of the Fourier treatment, over the range $-t_1$ to $+t_1$ of a function zero from $-t_1$ to 0, and equal to $f(t)$ from $t=0$ to $t=+t_1$, as t_1 is made indefinitely great. In calculating Q in that case, it is only necessary to take account of the particular integral (forced vibration), for the complementary function (free vibration) may be regarded as having died out during the interval $-t_1$ to zero. Note that $\int_0^\infty Q^2 dt$ is the integrated response of any square-law detector, *e. g.* a crystal, or valve detector without heterodyne, or the total heat generated in a resistance, and hence the throw of a thermocouple-galvanometer.

A general result may be deduced from (3). If two LRC assemblies have Y_q identical for a particular branch, for all values of q, Q in that branch, due to a pulse E, is in each case identically the same function of t.

In particular, for two simple circuits, $L_1 R_1 C_1$, $L_2 R_2 C_2$, mutual inductance M, the current produced in (2) due to the induced voltage E in (1) is identically that produced in (1) by the pulse E induced in (2), whatever may be the values of $L_1 R_1 C_1$, $L_2 R_2 C_2$, and M.

In the case of three inductively coupled circuits, a voltage pulse in the first produces in the last exactly that current produced in the first by the same pulse acting in the last.

The current in the final element of a chain of infinitely weakly coupled circuits is unaltered in form by changing the order of the circuits, and keeps its magnitude if the (infinitesimal) product of the mutual inductances remains the same.

We have seen that $\int_0^\infty Q^2 dt$ may be regarded as a measure of the response of a wireless receiver. We shall use (4) to compute the response to the pulses used to represent atmospherics, and also to pulses of the very special, approximately-periodic type called morse signals. It is therefore necessary to examine X_q as a function of q for several types of pulse.

II. PERIODOGRAMS OF COMMON ANALYTICAL PULSE-FORMS.

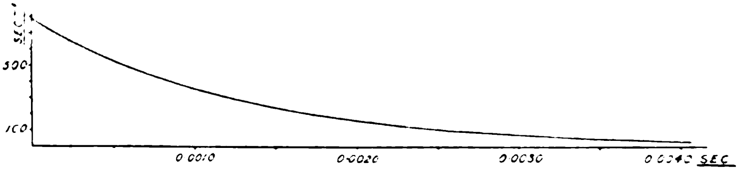
As a basis of comparison of different types of pulse, $E=f(t)$, we shall mention $\int_0^\infty E\,dt$ and $\int_0^\infty E^2\,dt$, as, according to circumstances, it may be of interest to compare equal charges, or equal energies.

(1) The Aperiodic pulse, $E=E_0\epsilon^{-\alpha t}$, lasting from $t=0$ to $t=+\infty$.

$$\int_0^\infty E\,dt=\frac{E_0}{\alpha},\quad \int_0^\infty E^2\,dt=\frac{E_0^2}{2\alpha}.$$

$$|X_q|^2=\frac{E_0^2}{(\alpha^2+q^2)}\text{ vanishing for } q=\infty \text{ as } q^{-2}.\quad\text{(Figs. 1 \& 11.)}$$

Fig. 1.



$$\frac{E}{C}=788\epsilon^{-788t}\text{ sec}^{-1}.\quad C=\int_0^\infty E\,dt=\text{constant}\left(\frac{\text{volt}}{\text{metre}}\text{ sec.}\right).$$

$$\alpha=250\pi=788.$$

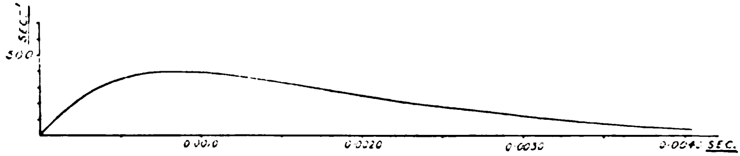
(2) $E=E_0(\epsilon^{-\alpha t}-\epsilon^{-2\alpha t})$ from $t=0$ to $t=+\infty$.

$$\int_0^\infty E\,dt=\frac{E_0}{2\alpha},\quad \int_0^\infty E^2\,dt=\frac{E_0^2}{12\alpha}.$$

$$|X_q|^2=\frac{\alpha^2E_0^2}{(\alpha^2+q^2)(4\alpha^2+q^2)}\text{ vanishing for } q=\infty \text{ as } q^{-4}.$$

(Figs. 2 & 11.)

Fig. 2.



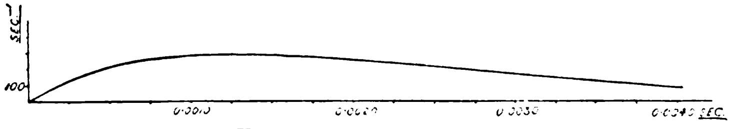
$$\frac{E}{C}=1576\left(\epsilon^{-788t}-\epsilon^{-1576t}\right)\text{ sec}^{-1}.$$

(3) $E=E_0\alpha t\epsilon^{-\alpha t}$ from $t=0$ to $t=+\infty$.

$$\int_0^\infty E\,dt=\frac{E_0}{\alpha},\quad \int_0^\infty E^2\,dt=\frac{E_0^2}{4\alpha}.$$

$$|X_q|^2=\frac{\alpha^2E_0^2}{(\alpha^2+q^2)^2}\text{ vanishing for } q=\infty \text{ as } q^{-4}.\quad\text{(Figs. 3 \& 11.)}$$

Fig. 3.



$$\frac{E}{C}=788^2t\,.\,\epsilon^{-788t}\text{ sec}^{-1}.$$

(4) The isolated half-sine wave,

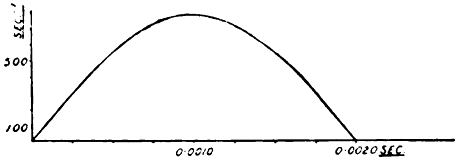
$$E = E_0 \sin pt \text{ from } t=0 \text{ to } t=\pi/p.$$

$$\int_0^\infty E\,dt = \frac{2E_0}{p}, \quad \int_0^\infty E^2\,dt = \frac{E_0^2 \cdot \pi}{2p},$$

$$|X_q|^2 = \frac{4p^2 E_0^2 \cos^2 \frac{\pi}{2} q/p}{(q^2-p^2)^2} \text{ vanishing for } q=\infty \text{ as } q^{-4}.$$

(Figs. 4 & 11.)

Fig. 4.



$$\frac{E}{C} = 788 \sin 1576t \,.\, \sec^{-1}. \qquad p = 500\pi = 1576.$$

(5) The "sensibly innocuous" pulse of Moullin*,

$$E = E_0 (\sin pt - \tfrac{1}{3} \sin 3pt) \text{ from } t=0 \text{ to } t=\pi/p.$$

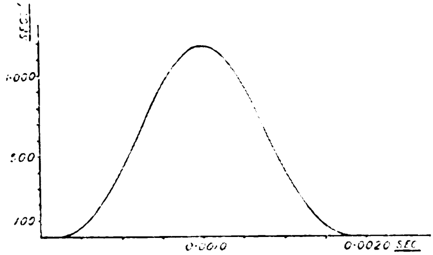
At both these times, all the derivatives up to the third are zero.

$$\int_0^\infty E\,dt = \frac{16}{9}\frac{E_0}{p}, \quad \int_0^\infty E^2\,dt = \frac{14\pi}{27p}E_0^2.$$

$$|X_q|^2 = \frac{256 p^6 E_0^2 \cos^2 \frac{\pi}{2} q/p}{(q^2-p^2)^2 (q^2-9p^2)} \text{ vanishing for } q=\infty \text{ as } q^{-8}.$$

(Figs. 5 & 11.)

Fig. 5.



$$\frac{E}{C} = \frac{9}{16} = 1576 (\sin 1576t - \tfrac{1}{3} \sin 4728t).$$

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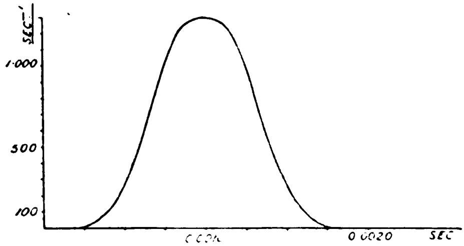
[*] J. I. E. E. No. 328, vol. lxii. p. 356, April 1924. E. B. Moullin, M.A., "Atmospherics and their effect on Wireless Receivers."

(6) $E = E_0(\sin pt - \frac{1}{2}\sin 3pt + \frac{1}{10}\sin 5pt)$ from $t=0$ to $t=\pi/p$. At both these times, all the derivatives up to the 5th are zero.

$$\int_0^\infty E\,dt = \frac{128}{75}\,\frac{E_0}{p}, \quad \int_0^\infty E^2\,dt = \frac{689\pi}{1500}\,\frac{E_0^2}{p}.$$

$$|X_q|^2 = \frac{384^2 . p^{10} . E_0^2 . \cos^2\frac{\pi}{2}q/p}{(q^2-p^2)^2(q^2-9p^2)^2(q^2-25p^2)^2}$$ vanishing for $q=\infty$ as q^{-12}. (Figs. 6 & 11.)

Fig. 6.



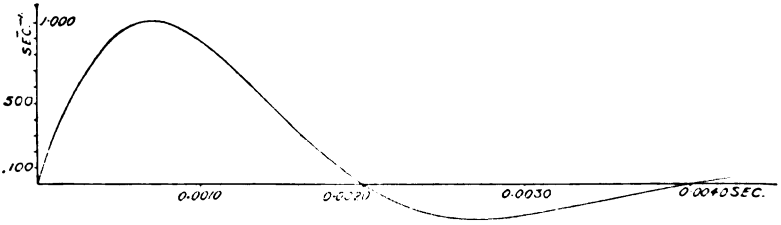
$$\frac{E}{C} = 925(\sin 500\pi t - \tfrac{1}{2}\sin 1500\pi t + \tfrac{1}{10}\sin 2500\pi t).$$

(7) The exponentially damped sine wave $E = E_0\epsilon^{-\alpha t}\sin pt$, from $t=0$ to $t=+\infty$.

$$\int_0^\infty E\,dt = \frac{p}{p^2+\alpha^2}E_0, \quad \int_0^\infty E^2\,dt = \frac{p^2E_0^2}{4\alpha(p^2+\alpha^2)}.$$

$$|X_q|^2 = \frac{p^2E_0^2}{(\alpha^2-q^2+p^2)^2+4\alpha^2q^2}$$ vanishing for $q=\infty$ as q^{-4}. (Fig. 7.)

Fig. 7.



$$\frac{E}{C} = 1{\cdot}25 \times 500\pi \times \epsilon^{-250\pi t}\sin 500\pi t\ \text{sec}^{-1}.$$

This function is similar to the resonance curve of an LRC circuit, having a maximum at $q=p$. Writing $\alpha = p\delta/2\pi$, the form of $|X_q|^2$ is given near $q=p$ when $\delta << 1$, by the approximation

$$\frac{|X_{p+\Delta p}|^2}{|X_p|^2} \doteq \frac{\left(\frac{\delta}{2\pi}\right)^2}{\left(\frac{\Delta p}{p}\right)^2 + \left(\frac{\delta}{2\pi}\right)^2}, \quad . \quad . \quad . \quad (5)$$

also

$$\frac{|X_p|^2}{\int_0^\infty E^2 dt} \doteq \frac{1}{\alpha} = \frac{2\pi}{\delta p}$$

—a result strongly suggesting the damped-wave resonance formulæ of Bjerknes, Brandes, Mandelstam and Papalexi and others. We shall return to this later.

(8) The exponentially damped cosine wave $E = E_0 \epsilon^{-\alpha t} \cos pt$ from $t=0$ to $t=+\infty$.

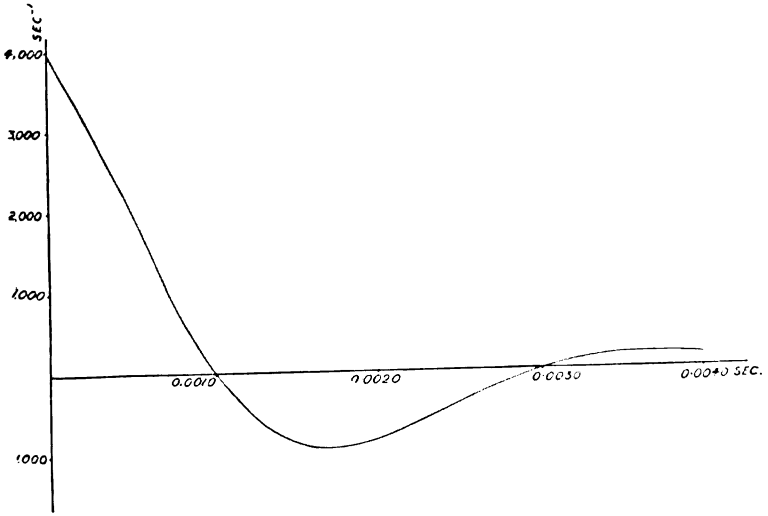
$$\int_0^\infty E\,dt = \frac{\alpha}{p^2+\alpha^2} E_0, \quad \int_0^\infty E^2 dt = \frac{2\alpha^2+p^2}{4\alpha(p^2+\alpha^2)} E_0^2.$$

$$|X_q|^2 = \frac{(\alpha^2+q^2)E_0^2}{(\alpha^2-q^2+p^2)^2+4\alpha^2q^2}$$ vanishing for $q=\infty$ as q^{-2}.

(Fig. 8.)

The same equation (5) may be deduced.

Fig. 8.



$\frac{E}{C} = 1250\pi \,.\, \epsilon^{-250\pi t} \,.\, \cos 500\pi t \,.\, \sec^{-1}.$

{The ordinates are on half the scale of the other figs.}

(9) The linearly damped sine wave.

$E=E_0(1-\beta t)\sin pt$ lasting from $t=0$ to $t=\beta^{-1}$.

If we assume $p=\pi m\beta$ (m half-oscillations)

$$\int_0^\infty E\,dt=\frac{E_0}{p},\quad \int_0^\infty E^2dt=E_0^2\left[\frac{2p^2-3\beta^2}{12\beta p^2}\right],$$

which $=E_0^2.\dfrac{8\pi^2m^2-3}{24\pi mp}\doteqdot\dfrac{\pi m}{3p}.E_0^2 \quad (m>>1)$.

$$|X_q|^2=\frac{p^2E_0^2}{(q^2-p^2)^2}\left[1-\frac{4pq\sin\frac{\pi mq}{p}}{(q^2-p^2)}\cos\pi m+\frac{8p^2q^2}{(q^2-p^2)^2}\left[1-\cos\frac{\pi mq}{p}\cos\pi m\right]\right]$$ vanishing

for $q=\infty$ as q^{-4}.

For

$$q=p,\quad \frac{|X_p|^2}{\int_0^\infty E^2dt}=\frac{3}{2p}.\frac{4\pi^2m^2+1}{8\pi^2m^2-3}.\pi m,\quad \doteqdot\frac{3\pi m}{4p}.$$

For an exponentially damped sine-wave (7) the same quantity is $2\pi/p\delta$. Thus if two waves of types (9) and (7) have the same total energy,

$$\frac{|X_p|^2\text{ linear}}{|X_p|^2\text{ exponential}}=\frac{3m\delta}{8}.$$

The waves start alike if $m\delta=1$.

Thus if the action of a spark-gap is to rise in resistance during the later stages of the oscillation in such a way as to produce linear damping, with the initial damping due to the circuit resistance, the ratio

$$\frac{\text{Energy density at Pulsatance}}{\text{Total Energy}}$$

is the same as if the spark-gap did not do this, but δ were increased in the ratio 8 : 3.

(10) The infinitely short pulse ("high frequency ripple").

$\text{Lt}_{\delta t=0}$ of $\int_0^{\delta t}E\,dt=I$, and E zero except from $t=0$ to $t=\delta t$.

$\int_0^\infty E^2dt$ is infinite.

$|X_q|^2=I^2$. This type thus has a constant distribution over the whole spectrum, independent of frequency.

Periodograms of Typical Morse Signals.

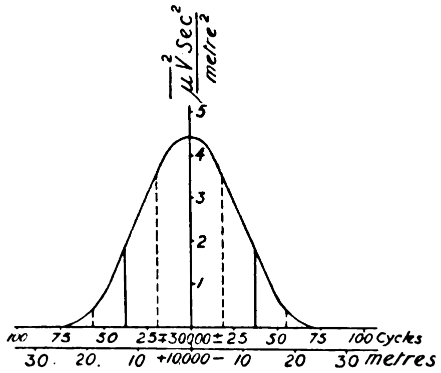
(11) One C.W. dot.

$$E = E_0 \sin pt \text{ from } t=0 \text{ to } t=\frac{2m\pi}{p}.$$

(m complete oscillations).

$$|X_q|^2 = \frac{4p^2E_0^2\sin^2\pi mq/p}{(q^2-p^2)^2}, \quad |X_p|^2 = \frac{\pi^2m^2}{p^2}E_0^2. \quad \text{(Fig. 9.)}$$

Fig. 9.



Relative values of contained energy at different frequencies for an infinite succession of C.W. Dots.
Full drawn: synphased. Broken: antiphased.
$\lambda = 10{,}000$ metres. 400 oscillations per Dot (95 words per minute).
The curved line is the periodogram for one dot.
Maximum received field strength 10 μV/metre.

(12) Two C.W. dots (synphased).

$E = E_0 \sin pt$, zero, $E_0 \sin pt$, from $t=0$ to $t=\frac{2m\pi}{p}$, $\frac{2m\pi}{p}$ to $\frac{4m\pi}{p}$, $\frac{4m\pi}{p}$ to $\frac{6m\pi}{p}$ respectively, and zero before and after.

$$|X_q|^2 = \frac{16p^2E_0^2}{(q^2-p^2)^2}\sin^2\frac{\pi mq}{p}\cos^2\frac{2\pi mq}{p},$$

$$|X_p|^2 = \frac{4\pi^2m^2}{p^2}E_0^2. \qquad \text{(Fig. 12.)}$$

(13) Two antiphased C.W. dots.

$E=E_0\sin pt$ zero, $-E_0\sin pt$, at the same times as above.

$$|X_q|^2=\frac{16p^2E_0^2}{(q^2-p^2)^2}\sin^2\frac{\pi mq}{p}\,.\,\sin^2 2\pi mq/p,\qquad |X_p|^2=\text{zero}.$$

(Fig. 12.)

(14) An infinite succession of synphased C.W. dots.

$E=E_0\sin pt$, or zero, alternately with note pulsatance, $z=p/4m$, $2m$ complete oscillations in a dot.

$$|X_{kz}|^2=\frac{4p^2E_0^2\sin^2 k\pi/2}{(p^2-k^2z^2)^2},\qquad \text{(Fig. 9.)}$$

in which k is a positive integer. The energy is reduced to that of one dot.

(15) An infinite succession of antiphased C.W. dots.

$E=E_0\sin pt$, zero, $-E_0\sin pt$, zero, alternately.

Note pulsatance $z=p/4m$, $2m$ complete oscillations in a dot.

$$|X_{kz}|^2=\frac{16p^2E_0^2\sin^2 k\pi/2}{(p^2-k^2z^2)^2}\sin k\pi/4,\qquad \text{(Fig. 9.)}$$

where k is a positive integer. The energy is reduced to that of one dot. For this and the previous case $|X_q|^2$ for values of $q\neq kz$ is zero.

On the Repetition of a Pulse.

Suppose the pulse E to occur n times at regular intervals (note pulsatance z). Let ${}_1X_q$ be the periodogram of $E=f(t)$, occurring once.

Then ${}_nX_q$, that of

$$E=\underset{\substack{t=0\\ \text{to } t=\infty}}{f(t)}+\underset{\substack{t=2\pi/z\\ \text{to } t=\infty}}{f\left(t-\frac{2\pi}{z}\right)}+\dots+\underset{\substack{t=\frac{2\pi(n-1)}{z}\\ \text{to } t=\infty}}{f\left(t-\frac{2\pi(n-1)}{z}\right)}$$

is given rigidly by

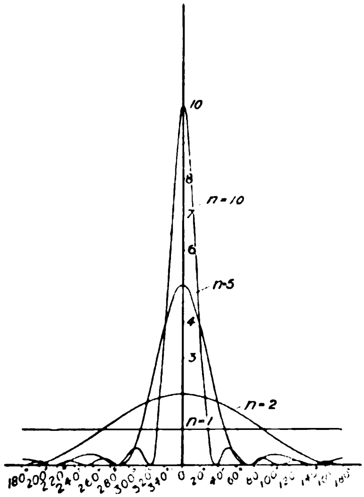
$${}_nX_q={}_1X_q\left[1+\epsilon^{2\pi i\frac{q}{z}}+\epsilon^{2\pi i\,.\,\frac{2q}{z}}+\dots+\epsilon^{2\pi i\,.\,\overline{n-1}q/z}\right],$$

and it follows that

$$|{}_nX_q|^2=|{}_1X_q|^2\,.\,\frac{\sin^2 n\pi q/z}{\sin^2\pi q/z}.$$

The periodic curve $\dfrac{\sin^2 n\pi q/z}{n\sin^2\pi q/z}$ is plotted for various values of n in fig. 10. These curves, considered as multipliers, acting on $|X_q|^2$, show the effect of regular repetition of a pulse, in concentrating the energy-density round those values of pulsatance which are harmonics of the note-pulsatance.

Fig. 10.



$$\frac{|{}_nX_q|^2}{n\,|{}_1X_q|^2} = \frac{\sin^2 \pi q/2}{n \sin^2 \pi q/2}$$ plotted against $q/90 \times 360°$.

Family of Curves for $n=1, 2, 5, 10$.

On the Periodogram of a Pulse and that of its Envelope.

If a pulse may be represented as $\phi(t) \sin pt$ or $\phi(t) \cos pt$, we shall call $\phi(t)$ the envelope of the pulse. There is a simple relation between the periodogram of a pulse, X_q, and that of its envelope χ_q.

If $X_q = a_q + ib_q$ and $\chi_q = \alpha_q + i\beta_q$, the following relations exist, for

$$f(t) = \phi(t) \sin pt,$$

$$a_q = \tfrac{1}{2}(\beta_{p+q} + \beta_{p-q}) \text{ and } b_q = \tfrac{1}{2}(\alpha_{p-q} - \alpha_{p+q}).$$

For

$$f(t) = \phi(t) \cos pt,$$

$$a_q = \tfrac{1}{2}(\alpha_{p+q} + \alpha_{q-p}) \text{ and } b_q = \tfrac{1}{2}(\beta_{p+q} + \beta_{q-p}).$$

Now in morse signal pulses such as the C.W. dot, the exponentially and linearly damped sine wave, for values of q near to p, α_{p+q} and β_{p+q} are $<< \alpha_{p-q}$ and β_{p-q}, therefore approximately

$$|X_{p+\Delta p}| = \tfrac{1}{2}\ \chi_{\Delta p}|.$$

Thus the periodogram of the envelope determines the shape of the principal peak in that of the pulse. It gives a generalization of the so-called "side-bands" of a transmission.

If we apply this reasoning to a pulse of type (7) we have (see type (1)),

$$\frac{|X_{p+\Delta p}|^2}{|X_p|^2}=\frac{|\chi_{\Delta p}|^2}{|\chi_0|^2}=\frac{\alpha^2}{(\Delta p)^2+\alpha^2}=\frac{\left(\frac{\delta}{2\pi}\right)^2}{\left(\frac{\Delta p}{p}\right)^2+\left(\frac{\delta}{2\pi}\right)^2},$$

an elegant way to deduce Bjerknes' law.

The General Type.

Let $E=f(t)$ from $t=0$ to $t=\infty$, and let f satisfy the conditions sufficient to warrant the validity of the Fourier development.

Consider the general integral

$$Z=\int f(t)\,.\,\epsilon^{iqt}\,.\,dt.$$

Partial integration gives

$$Z=\epsilon^{iqt}\left(\frac{-i}{q}\right)\left[f+\left(\frac{i}{q}\right)f'+\frac{i^2}{q^2}f''+\ldots+\left(\frac{i}{q}\right)^n f^n\right]$$
$$+\left(\frac{i}{q}\right)^{n+1}\int f^{n+1}(t)\,.\,\epsilon^{iqt}\,.\,dt$$
$$=\epsilon^{iqt}\left[\frac{f}{D+iq}\right]_n(t)+\left(\frac{i}{q}\right)^{n+1}\int\epsilon^{iqt}\,.\,f^{n+1}(t)\,.\,dt,$$

where D denotes d/dt. The interpretation to be put on this form is that it must be expanded as a power-series in D which operates on $f(t)$. Insertion of the limits of 0 and ∞ gives

$$X_q=\left[\frac{-f}{D+iq}\right](0).$$

When the function or a derivative shows discontinuities at $t=t_1$,

$$X_q=\left[\frac{-f}{D+iq}\right](0)+\left[\frac{-f}{D+iq}\right](t_1+0)-\left[\frac{-f}{D+iq}\right](t_1-0).$$

Thus, in the case of a function continuous with all its derivatives from $t=0$ to $t=\infty$, the periodogram is entirely determined by the function and its derivatives at $t=0$, being in fact

$$X_q=\frac{i}{q}\left[f(0)+\left(\frac{i}{q}\right)f'(0)+\left(\frac{i}{q}\right)^2 f''(0)+\ldots+\ldots\right].$$

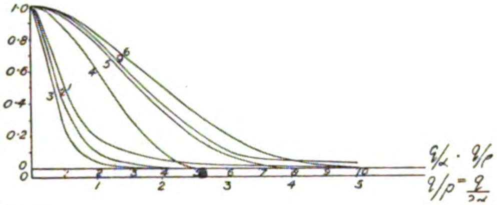
The series is generally found to be rapidly convergent with large values of q, and it is evident that the more of the earlier derivatives are zero, the higher is the order of q^{-1}, to which $|X_q|$ is proportional, with infinite q.

Approximate Pulse Forms.

It follows that if the form of a pulse is only approximately known (as, for instance, from an oscillogram), it will not be legitimate, having represented the pulse by an approximate mathematical expression, to deduce from that expression the behaviour of $|X_q|$ with infinite q, and the values obtained for $|X_q|$ will decrease in reliability as q is increased. We shall, however, find that in discussing the elimination of atmospheric pulses while receiving signals on any one frequency, the order of $|X_q|$ with infinite q is unimportant.

$|X_q|^2$ for different types of pulse is plotted in figs. 1–6, 9, 11, 12, and $|X_q|^2$ for great values of q is given in Table I.

Fig. 11.



$\frac{|X_q|^2}{C^2}$, for different pulse forms (1, 2, 3, 4, 5, 6, 9)

based upon $\int_0^\infty E\,dt = C = \text{Constant}$.

As a basis for comparison $\int_0^\infty E\,dt$ has been taken as constant (c), and $\alpha = p/2$, $\beta = p/2$.

It is clear that the principal features distinguishing the periodograms of pulses which might be used to represent atmospherics from those of the pulses used in wireless signalling are (1) that the principal maxima of the former occur at lower values of q than those of the latter; (2) that the principal maxima of the morse signals are very much more sharply defined.

In fact, while static may be said to "have all wave-lengths, though principally long ones," signals "on" a certain wave-length have all but a very small portion of their action concentrated near that wave-length.

We have now to consider X_q in conjunction with Y_q.

TABLE I.

Pulse No.	$E=f(t)$		$(X_q)^2, q=3\times10^4$ $\lambda=10$ km.	$(X_q)^2, q=3\times10^5$ $\lambda=1$ km.
			unit: $\left(\frac{\text{volt. second}}{\text{metre}}10^{-10}\right)^2$	
(1)	$E=E_0\epsilon^{-at}$ $t=0$ to $t=+\infty$ $a=0$ $E_0=1\frac{\text{volt}}{\text{metre}}$			
Simple Discontinuity in E			$2{\cdot}8145\times10^9$	$2{\cdot}8145\times10^7$
(4)	$E=E_0\sin pt$ $t=0$ to $t=\pi/p$ $E_0=1\frac{\text{volt}}{\text{metre}}$	$\frac{p}{2\pi}\approx\frac{500}{\text{sec.}}$ $p^2=10^7$		
Half Sine Wave			$1{\cdot}2854\times10^6$	$1{\cdot}2854\times10^2$
(5)	$E_0=E_0(\sin pt-\frac{1}{3}\sin 3pt)$ $t=0$ to $t=\pi/p$ $E_0=1\frac{\text{volt}}{\text{metre}}$	$p^2=10^7$		
"Innocuous Pulse" of Moullin.			$6{\cdot}5506$	$6{\cdot}5142\times10^{-8}$
(7)	$E=E_0\epsilon^{-\frac{1}{2}pt}\sin pt$ $t=0$ to $t=+\infty$ $E_0=1\frac{\text{volt}}{\text{metre}}$	$p^2=10^7$		
Damped Sine Wave			$3{\cdot}9625\times10^5$	$3{\cdot}9615\times10^1$
(11)	$E=E_0\sin pt$ $t=0$ to $t=800\,\pi/p$ $E_0=1\frac{\text{microvolt}}{\text{metre}}$	$p=2\pi\times3\times10^4$		
C.W. Dot: 400 oscillations.		$\lambda=10$ km.	$4{\cdot}444\times10^3$	$1{\cdot}1487\times10^{-8}$
C.W. Dot as above, but with $p=2\pi\times3\times10^5$.		$\lambda=1$ km.	$1{\cdot}1487\times10^{-4}$	$4{\cdot}4444\times10^1$

The Complete Sine Wave $E=E_0\sin pt$, $t=0$ to $t=2\pi/p$ gives figures identical with those of the half-sine wave.

In cases where $(X_q)^2$ is zero at 10 km. or 1 km. the average value near those wave-lengths is given.

III. THE RESPONSE OF A RESONANT SYSTEM.

Formulæ have been developed, giving the response $\left(\int_0^\infty \text{current}^2 . dt\right)$ of receiving systems of given decrement to transmissions with logarithmic decay, by Bjerknes and others, of type

$$\int_0^\infty Q^2 dt \propto \frac{1}{\delta_1\delta_2}\cdot\frac{\delta_1+\delta_2}{\left(\frac{\Delta p}{p}\right)^2+\left(\frac{\delta_1+\delta_2}{2\pi}\right)^2}.$$

This formula assigns to transmitter and receiver (interchangeable) flatnesses of tuning, of particular shape, and of effective width proportional to the decrement. It has often been asked if similar flatnesses might not be assigned to transmissions with any kind of damping.

This is done by (4)

$$\pi\int_0^\infty Q^2 dt = \int_0^\infty |X_q|^2 . |Y_q|^2 . dq.$$

The interchangeable flatnesses of transmission and reception are $|X_q|$ and $|Y_q|$, and they are in a sense additive. Thus we see that the periodogram gives the flatness of tuning of a transmission in exactly that sense in which the receiver resonance curve gives the flatness of tuning of reception. If the receiver is infinitely selective, there is a flatness of tuning given by the periodogram alone.

Indeed, it may be seen at once that the free vibration (complementary function) of a quiescent LC circuit having no resistance is given for any pulse form in magnitude and phase by the complex $L^{-1}\left[\frac{-f(0)}{D+iq_0}\right]$, $\left(q_0=\frac{1}{\sqrt{LC}}\right)$, which is X_{q_0}/L. The free vibration in the case of all pulses save the infinitely long, centrally tuned sine wave, may be regarded as contributing the whole of $\int_0^\infty Q^2 dt$ in the case of $R=0$.

We have to consider circuits of finite decrement, and also circuits having resonance curves of any shape whatever.

Consider $|Y_q|^2$ (Q, E) for an LRC circuit of decrement δ $\left(\text{defined as } \frac{R}{\pi}\sqrt{\frac{C}{L}}\right)$, where Q is the current and E the induced voltage. Let the pulse be of the type (10)

$$|Y_q|^2=\frac{q^2C^2}{(1-q^2LC)^2+q^2C^2R^2}$$

and

$$\int_0^\infty Q^2 dt = \frac{1}{\pi}\int_0^\infty |X_q|^2 . |Y_q|^2 . dq$$

$$= \frac{I^2}{\pi}\int_0^\infty |Y_q|^2 \, dq,$$

integrating

$$\int_0^\infty Q^2 dt = \frac{I^2}{\pi} . \frac{1}{\sqrt{LC}} . \frac{\pi^2}{2\delta} .$$

The current² response is therefore finite, and $\propto \delta^{-1}$, even though the pulse, acting on a pure resistance, would supply infinite energy.

The current² response for a long, centrally-tuned sine wave $\propto \delta^{-2}$, so the ratio

$$\frac{\text{received signal energy}}{\text{received static energy}} \propto \delta^{-1}$$

for pulse (8), and it is easy to see that an alteration of $|X_q|^2$ for values of q far from $q_0\left(=\frac{1}{\sqrt{LC}}\right)$ will be without effect if δ is sufficiently small.

For $\delta < < 1$, the result will be true for any atmospheric pulse. By employing a sufficiently low decrement, the signal : static ratio might be made as great as is desired.

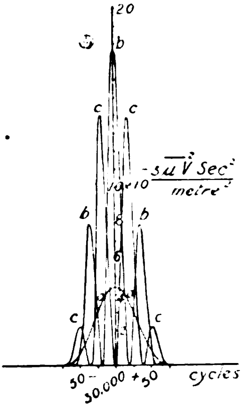
It is therefore necessary to discuss the ratio in the case when selectivity is definitely limited, to prevent "ringing" or distortion of signals.

We have no direct knowledge of the initial amplitude and form of the free oscillations, in a system of arbitrary resonance curve ; the amount of distortion may, however, be deduced in a simple way. Consider the response $\left(\int_0^\infty Q^2 dt\right)$ to a signal consisting of two dots, separated by a space, the second having an arbitrary phase relationship with the first.

If "ringing" is present, the response will be dependent on this phase relationship, but if no such dependence occurs, Q due to the first dot must necessarily have died out during the space. Periodograms of two spaced dots, syn- and anti-phased, are given in fig. 12, in which it will be noticed that (syn) the peak of $|X_q|^2$ is raised (4 : 1) and narrowed, and (anti) the peak splits up into two with a central zero. If (anti) both these peaks fall under the flat top of the $|Y_q|^2$ peak, the response will be approximately the same as in the syn case. If the $|Y_q|^2$ peak is as sharp as the principal peak in the syn case, the response will exceed that in the anti-case considerably.

Another aspect of the matter is obtained by comparing two resonance curves which have (*a*) the same peak height—and therefore receive long dashes equally; (*b*) the same total area—and therefore give equal responses to pulses of type (10). The best will be that which gives the greatest response to an isolated dot.

Fig. 12.



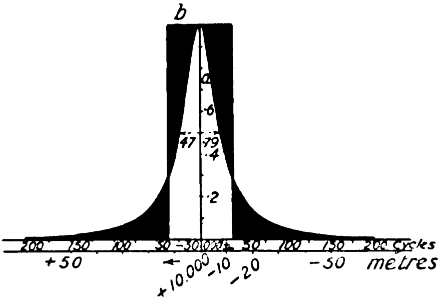
$|X_q|^2$ as a function of $\nu = \frac{q}{2\pi}$ in the neighbourhood of $\nu = 30{,}000$ (10 km.).

a. Periodogram of one C.W. Dot.
b. „ two synphased C.W. Dots.
c. „ two antiphased C.W. Dots.
Wave-length of transmissions 10,000 metres.
Number of oscillations in one dot 400.
($m = 400$, 95 words per minute.)
Maximum field-strength at receptions 10 μV/metre.

Clearly a pointed peak and a rounded foot are bad features, and though the nature of the argument is such as to preclude an absolutely final decision, the optimum shape would appear to be $|Y_q|$ zero except over a range $q_0 \pm \Delta_q$, where Δ_q is dependent on the allowable distortion. A particular case is shown in fig. 13 where a simple LRC resonance curve is shown of $\delta = \cdot 005$, and also a square-topped, vertical-sided curve of equal height and area.

We have considered a transmitter in which the aerial current assumes its steady-state value at the instant the key is depressed. In high-speed signalling without spacing waves, it may be necessary to take account of the slow building up of the oscillations. This may be done by plotting periodograms from the oscillograms of dots, by the envelope formula, or by superposing the antenna resonance curve on that of the receiver, though the latter method is approximate only, in view of non-linearity in the behaviour of triode and other generators.

Fig. 13.



(Width (square-topped) = width of $|Y_q|^2$, (LRC circuit), at half height) × $\frac{\pi}{2}$.

The periodogram of two anti-dots having 400 oscillations is shown (fig. 12). It will be seen that the distortion is considerably less with the square-topped curve.

Reception of a Repeated Pulse.

It has been shown in II. that the energy of a transmission such as the "running dots" of a wheatstone transmitter, or the successive trains of a musical spark set, is concentrated in narrow bands round the harmonics of the note-pulsatance. Such a transmission may be said to be distorted on reception when the principal contribution to the response arises from a peak of the $|Y_q|^2$ curve of width comparable with the note-pulsatance.

At this point spark-signals give a scratchy sound in telephones, for the response then shows marked dependence on the note-pulsatance—that is, on the (erratic) phase relationship between successive sparks. The position of the harmonic ordinates is shown in fig. 9 for the case of syn- and anti-phased dots, the spaces being equal to the dots in duration.

Unless the permissible distortion is very great, the receiver resonance curve must be approximately as broad as the principal peak of the periodogram of one dot; again, a pointed peak and a rounded foot are bad features as far as the signal : static ratio is concerned.

Heterodyne Detection and Note Filtration.

By employing a sufficiently powerful heterodyne of pulsation N, the detector output due to a sustained signal A cos q_0t may be made as nearly as is desired,

$$KA\cos(q_0+N)t + KA\cos(q_0-N)t,$$

where K is a constant depending on the detector and the heterodyne strength. Imagine the pulse $E=f(t)$ analysed as a Fourier series over a very long period T. If this period is made sufficiently long, the detector output, Q, due to the pulse, computed as the sum of the outputs due to each term of the series will be independent of small variations of T. We may therefore suppose that T contains an integral number of heterodyne oscillations.

All the terms in the output, Q, will therefore be harmonic with respect to T, and $\int_0^\infty Q^2dt$ will be given by the sum of the contributions which each harmonic would make, in the absence of the rest.

Any one term in the output arises from two terms in the detector input. Suppose that the note selection following detection is such that only a particular band of pulsatances, q_a to q_b, in the detector output need to be considered. This band will arise from two bands (q_a+N) to (q_b+N) and (q_a-N) to (q_b-N) in the detector input.

If the selection preceding detection is such that only one of these bands need be considered, the terms lying within this band contribute independently to the detector output. Then $\int_0^\infty Q^2dt$ may be computed by incorporating the high- and low-frequency selectivities into one resonance curve where $\frac{\text{Output}-\text{mean square}}{\text{Input}-\text{mean square}}$ is plotted for various values of q.

If, therefore, we possess filter circuits which pass appreciably only pulsatances lying within a given band, we can in effect narrow that band by heterodyning before performing the final selection. It is, however, necessary to precede heterodyning by selection so good that a given note pulsatance can arise appreciably from one H.F. pulsatance only.

We have assumed that resonant systems can be realized which have peaks with sensibly vertical sides and flat tops. Cascaded selections in circuits with moderate decrement (Campbell filters) produce a resonance curve approximating more closely to this ideal than does one selection in a circuit of very low decrement; if the decrements are so chosen that the curves cross at particular values of q, and the curves are so scaled that the peak heights are identical, the cascaded-selection curve between these points is never lower, and outside them is never higher than the single-selection curve.

Circuits will readily suggest themselves in which $|Y_q|^2$ may be made proportional to any powers of q and q^{-1}, as q approaches zero and infinity. It should be noted that in computing $|Y_q|^2$ for q large, the increase in H.F. resistance due to skin effect, distributed capacity and radiation should be taken into account.

Triode assemblies in which the amplification is linear, and the retroaction insufficient to produce sustained oscillations, have the property that every possible free vibration has a finite, positive, damping exponent; the method is therefore applicable to non-oscillatory amplifiers, and the desirable cascading of selections, each of moderate decrement, may well take place in such amplifiers. It is a matter of complete indifference at what point in the system Antenna-Detector circuit the lowest decrement is placed. Two cases call for special attention: the so-called aperiodic antenna, and the closed coil aerial.

The Aperiodic Antenna.

An antenna of capacity C is earthed through a resistance R. The grid-filament of a triode is connected across R. We examine the grid voltage due to E,

$$|Y_q|^2 = 1 - \frac{1}{1+q^2C^2R^2},$$

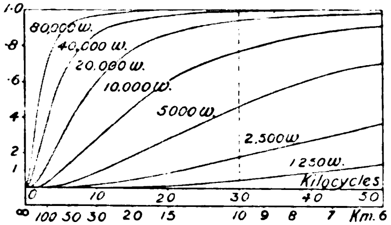
and is thus constant for q large, and tends to zero as q approaches zero. The signal : static ratio is therefore best, not when R is very large, but at some point such that $|Y_q|^2$ is appreciably less than 1. (See fig. 14.) The contribution to $\int_0^\infty Q^2 dt$ from higher values of q than q_0 is not appreciably altered; that from the lower values of q is lessened considerably.

The Closed Coil Aerial.

The pulse $E=f(t)$ acts in opposing senses on each limb, with a time lag of $t=-r/c$, where r is the distance between the limbs and c is the velocity of light, and the plane of the coil is perpendicular to the wave front. Then $|X_q|$ for the line-integral of electric force round the frame is thus obtained by multiplying $|X_q|$ of $f(t)$ by $2\sin qr/2c$.

Thus $\int_0^\infty Q^2dt$ for the open antenna is $\int_0^\infty |X_q|^2.|Y_q|^2.dq$, while for the closed coil it is $4\int_0^\infty |X_q|^2.|Y_q|^2.\sin^2 qr/2c.dq$.

Fig. 14.



$|Y_q|^2=1\frac{1}{1+q^2C^2R^2}$. $C=1\,m\mu F$.

Family of Curves for different R.

The frame is therefore fundamentally different from the open antenna in that the contribution to $\int_0^\infty Q^2dt$ from values of $q<\pi c/r$ is reduced. But if the decrement is sufficiently low, the only part of the contribution that need be considered is that arising from a band of width proportional to the decrement, centred round $q=q_0$ (signal pulsatance) over which the factor $\sin^2 qr/2c$ is approximately constant, and affects the signal and static responses equally.

Thus, apart from directivity, the low decrement frame gives approximately the same signal : static ratio as an open antenna of equal decrement. In the same way, the aperiodic antenna, if followed by a circuit of sufficiently low decrement, confers no appreciable advantage. It is only when the selectivity of the later stages is limited that there is a gain.

In the systems considered, though the shape of the resonance curve has been imagined entirely at our disposal, the ratio

$$\frac{\int_0^\infty Q^2dt\ (\text{signal})}{\int_0^\infty Q^2dt\ (\text{static})}$$

can only approach the ratio

$$\frac{|X_q|^2\,(\text{signal})}{|X_q|^2\,(\text{static})},$$

and can never exceed it.

On the Limiter-Selector Method.

In closing our brief survey of atmospheric elimination by linear selective methods, let us note one numerical example of the pitfalls awaiting those who would exceed the "ideal" signal : stray ratio by the employment of receivers having a limiting action.

Consider pulse (3)

$$E = E_0 \alpha t \epsilon^{-\alpha t}_{t=0 \text{ to } t=\infty}, \qquad |X_q|^2 = \frac{\alpha^2 E_0^2}{(\alpha^2+q^2)^2}.$$

Let this pulse act (a) on a circuit of decrement δ, where $\delta << 1$, tuned to q_0; (b) on a limiting device with a sharp or slightly rounded cut-off, after which the limited pulse acts on the low decrement circuit of (a).

In the case (b), if limiting occurs at t_1, where $\alpha t_1 << 1$, the pulse may be considered as approximately $E = E_0 \alpha t$ from $t=0$ to $t=t_1$, and $E_0 \alpha t_1$ until limiting ceases, and from that time till $t=\infty$, $E = E_0 \alpha t \epsilon^{-\alpha t}$. We will suppose t_1 to be several signal periods, $2\pi/q_0$.

The discontinuities introduced by limiting occur at an interval having no special relation to $2\pi/q_0$, the signal period. Therefore in computing $|X_{q_0}|^2$ according to the method outlined for the general type, we must compute $|X_{q_0}|^2$ for each discontinuity separately, and add the values so obtained. A lower limit to $|X_{q_0}|^2$ (limited) is obtained by considering only the first two discontinuities, in which the jumps of dE/dt are $+\alpha$ and $-\alpha$. Then $|X_{q_0}|^2$ (limited) is $2\alpha^2 E_0^2/q_0^4$, which exceeds slightly $2|X_{q_0}|^2$ (unlimited), (in practice, $\alpha << q_0$).

Further, if the limiter has a slightly rounded cut-off, provided the rounding of the discontinuity in dE/dt at t_1 is complete in an integral not greater than a half period of the signal (π/q_0), the effect on $|X_{q_0}|^2$ is small.

The act of limiting, then, has doubled $|X_{q_0}|^2$ and has therefore doubled $\int_0^\infty Q^2 dt$ in the low decrement circuit, and it may be seen that in the case of a pulse containing, when unlimited, only discontinuities in the higher derivatives, $|X_{q_0}|^2$ may be increased in an even greater ratio.

Though we have examined only one particular case, it is enough to show that considerable analysis is necessary before we can say with L. B. Turner[*] that, granted a suitable limiter, the limiter-selector method provides, even in theory, a solution of the atmospheric problem.

IV. CONCLUSION.

Means have been given for plotting the density of amplitude and square of amplitude of a non-periodic pulse over the wireless spectrum.

The response created in a resonant system of entirely arbitrary resonance curve has been examined, in terms of the periodogram of the pulse, or resonance curve of contained frequencies, and it has been shown that only a finite range of frequencies in the wireless spectrum are of practical importance.

The best form of resonance curve for the reception of morse signals and the elimination of interference has been shown to have vertical sides and a flat top; this implies a multiplicity of selecting circuits, the order of which is unimportant.

The benefit accruing from the use of the aperiodic antenna, and the loop antenna (apart from directivity) has been shown to be small. The paper demonstrates the existence of a maximum signal : stray ratio which can never be exceeded, with linear apparatus, and indicates a possible weakness of limiting systems.

In conclusion, we have pleasure in expressing our thanks to Professors B. van der Pol, W. H. Eccles, G. I. Taylor, C. L. Fortescue, and especially to Dr. A. Koerts, for their kind interest and criticisms, and to Mr. A. P. M. Fleming, C.B.E., M.I.E.E., M.Sc.Tech., Director of Research, Metropolitan-Vickers Electrical Company Limited, for his kind permission to publish this investigation.

Research Laboratories,
Metropolitan-Vickers Electrical Co. Ltd.,
Trafford Park, Manchester.

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[*] L. B. Turner, 'Outline of Wireless.'

LII. *A Proposed Test of the Space Quantization of Atoms in a Magnetic Field.* *By* ARTHUR EDWARD RUARK *and* G. BREIT *.

§ 1. THE experiment of Stern and Gerlach † shows that the space quantization of atoms is obeyed by the atoms of many elements. The technical difficulties of this experiment are so great that it is desirable to devise other means of testing the space quantization.

Further, the results of the Stern and Gerlach experiment yield only the component of the magnetic moment of the atom parallel to the field. This leaves a gap in our knowledge which is very undesirable for reasons which are well illustrated by considering Bohr's model of the helium atom. This model is paramagnetic, while helium gas is diamagnetic. To explain this, Bohr assumes the space quantization of normal helium to be such that all the atoms place themselves with their axes of angular momentum perpendicular to the field. There is thus no positive contribution to the susceptibility, and the gas is diamagnetic. If the Stern and Gerlach experiment for helium, assuming it possible, were to show that helium atoms are undeflected, it would not decide between the view of Bohr outlined above, and the view that the helium atom has no magnetic moment, and can take up any orientation whatever with respect to the field.

The fundamental question to be decided is whether properties of matter in bulk may be used. If such is the case the unidirectional stream of atoms may be dispensed with and the test for the space quantization can be conducted by means of any property of matter which has a vector character and which depends on the state of atoms in their normal energy level. Thus, if all atoms, say of helium, should be orientated with their axes of angular momentum perpendicular to the direction of the magnetic field, then we should expect helium to have a different dielectric constant depending upon whether the applied electric field is perpendicular or parallel to the applied magnetic field. Similarly the thermal conductivity or the viscosity might be supposed to be different, according as to whether the temperature or velocity gradient is perpendicular or parallel to the applied field.

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* Communicated by the Authors. Published by permission of the Director of the Bureau of Standards, Department of Commerce, and of the Director of the Department of Terrestrial Magnetism, Carnegie Institution of Washington.

† See Gerlach and Stern, *Ann. d. Phys.* lxxiv. p. 673 (1924), for bibliography.
Gerlach and Cilliers, *ZS. für Phys.* xxvi. p. 106 (1924).

Of course, if the atoms were orientated at random, the vector properties of the gas would be slightly different in directions parallel and perpendicular to the field, because of the Larmor precession. But the ratio of the change in any quantity measured first along and then across the field to the quantity itself is negligibly small in all cases of practical interest. Here we are speaking of effects due to the pseudo-crystalline state of the gas, caused by space quantization.

It may be possible to construct theories which will predict differences in the magnitude of such quantities as the dielectric constant, the refractive index, or the magnetic rotation of the plane of polarization, according as we adopt the hypothesis of space quantization or that of random orientation. However, it seems preferable to consider only the change of properties with direction in the magnetic field, since we are then independent of questionable theories.

§ 2. We must decide, therefore, whether it is rational for the consequences of space quantization to be applied to properties of matter in bulk. In the case of some properties the probability of an anisotropic nature with respect to the field seems very questionable. Thus in discussions of viscosity, the mean free path in various directions is the determining factor. When atoms collide the interactions may be supposed to be of such a radical character as to make the presence of the external magnetic field of no consequence. Similarly with thermal conductivity.

The case is different with such a property as the dielectric constant. The time which an atom spends between collisions is large compared with the time occupied by a collision, and the only essential condition therefore is that the space quantization should predominate over a random orientation during an appreciable portion of the time between two collisions.

Little information is available as to the time necessary for space quantization to set in. No evidence of lag was found in the experiment of Stern and Gerlach. Their test for the presence of undeflected atoms is very delicate, and in the case of silver all atoms are deflected. The difficulties of understanding the rapidity of orientation have been brought out by Einstein and Ehrenfest [*]. The other and less direct line of evidence comes from data on paramagnetism which appear to be in satisfactory agreement with the theory of space quantization, using the Bohr magneton as the quantum of magnetic moment [†].

If the Bohr magneton may be used in Pauli's manner for a material in bulk, then it is rational to expect space quantization to be applicable and it appears safe to say that orientation takes place in a small fraction of the time between collisions.

Such a state of affairs would occur in oxygen gas and NO. Similarly, paramagnetic salts must satisfy the space quantization conditions.

The evidence concerning the Bohr magneton may be criticised, however, as is done by Weiss [‡] from the purely experimental point of view, and also because the data of Wood and Ellett [§] on the polarization of resonance radiation seem to indicate that the time which is necessary for the establishment of space quantization in an excited state is of the same order of magnitude as the period of the Larmor precession in the magnetic field applied.

For weak fields the period of the Larmor precession is likely to be longer than the mean time between collisions. However, with fields of the order of 10,000 gauss the Larmor precession has a period of the order of $6 \,.\, 10^{-11}$ sec., which is smaller than the mean time between collisions of say helium, at atmospheric pressure ($\simeq 3 \times 10^{-10}$ sec.). We see therefore that with fields of reasonable strength, we can expect an anisotropic effect on the dielectric constant.

§ 3. We must discuss next the feasibility of obtaining anisotropic electric effects by the action of the magnetic field from the point of view of the reciprocity of action of these two fields. We can make use in this of the very lucid treatment of Klein [||] of the perturbations in the motion of an electron in a hydrogenic orbit under the simultaneous action of an electric and a magnetic field. The results of this treatment are these. Let us denote the electric and magnetic intensities by **E** and **H** respectively, and let

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[*] *ZS. für Phys.* xi. p. 31 (1922).

[†] W. W. Pauli, Jr., *Phys. Zeit.* xxi. p. 615 (1920). Epstein, Science, lvii. p. 532 (1923). Sommerfeld, *ZS. für Phys.* xix. p. 221 (1923). Dorfmann, *ZS. für Phys.* xvii. p 98 (1923). Weiss, *Journal de Phys.* iv, p. 153 (1923), and v. p. 129 (1924).

[‡] *Journal de Phys.* v. p. 129 (1924).

[§] Proc. Roy. Soc., A, ciii. p. 396 (1923).

[||] Oskar Klein, *ZS. für Phys.* xxii. p. 109 (1924).

$$\left.\begin{aligned} \mathbf{A} &= \frac{e}{2mc}\mathbf{H} + ek\,\mathbf{E}, \\ \mathbf{B} &= \frac{e}{2mc}\mathbf{H} - ek\,\mathbf{E}, \\ k &= \frac{3}{4\pi m a \omega}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (3)$$

Here e and m are the charge and mass of the electron; $2a$ is the major axis of the undisturbed orbit and ω the frequency of revolution of the electron, while c is the velocity of light. Defining two vectors

$$2\mathbf{U} = \mathbf{R} + k\mathbf{P},$$

$$2\mathbf{V} = \mathbf{R} - k\mathbf{P},$$

where **R** is the vector drawn from the nucleus to the electrical centre of the osculating orbit and where **P** is the angular momentum of the osculating orbit, the following relations hold:

$$\frac{d\mathbf{U}}{dt} = [\mathbf{A}, \mathbf{U}]$$

$$\frac{d\mathbf{V}}{dt} = [\mathbf{B}, \mathbf{V}].$$

These equations express the fact that the vectors **U**, **V**, rotate with the angular velocities **A**, **B**, respectively.

If **E** is sufficiently small compared with **H**, $\mathbf{A} \cong \mathbf{B}$ and the whole orbit may be thought of as precessing with the angular velocity $\frac{e}{2mc}\mathbf{H}$. Since we are concerned with quantization under these conditions, it is convenient for us to choose ωt, At, and $(A-B)t$ as the angular variables of the system. Calling these w_1, w_2, and w_3 respectively, the momentum associated with $(A-B)t$ is to satisfy the relation $J_3 = n_3 h$. If $A \rightarrow B$ the period corresponding to w_3 may become long in comparison with the mean time τ which the atom is likely to spend in an excited state [approximately the time constant of a radiating electron]. If such is the case, the quantization associated with J_3 is likely to be ineffective (by analogy with the case of the experiments of Wood and Ellett). Fields smaller than 1 volt/cm. make the time $> 2 \times 10^{-7}$ sec., and thus one may hope to obtain the effect of an electric field by considering the quantum states determined by the magnetic field and the small distortions in these states due to the electric field*.

Further, regardless of the magnitude of τ, if the period of w_3 is long in comparison with the period of w_2 we deal with a small Stark effect and a large Zeeman effect, and it is clear that each of the Zeeman components is subdivided into a number of Stark components. These correspond to different values of J_3 and to the same value of J_2. On account of the vector character of the expressions for **A** and **B** in terms of **E** and **H** there is in general an anisotropic property of each Zeeman term with respect to its Stark components depending upon whether the fields **E**, **H** are parallel or perpendicular to each other. Thus, *e. g.*, if **E** and **H** are perpendicular to each other, **A** and **B** are equal to each other in absolute value for small **E** so that the influence of w_3 is negligible, while if **E** and **H** are parallel this is not the case. The quantum nature of the Stark effect becomes apparent therefore in the longitudinal arrangement of fields before it is felt in the transverse position.

A difference in the dielectric constant in two directions implies double refraction for long waves. Double refraction for radiation in general is caused by the presence ot the magnetic field. In how far this refraction is a direct function of the orientation of the atom in the lowest energy state is difficult to say: the characteristics of higher states may also be involved. In the neighbourhood of absorption frequencies the effect merges with the Zeeman effect.

An experimental test of the ideas in § 1 and § 2 seems readily possible. The method of heterogeneous beats should be capable of revealing variations in the dielectric constant of helium with direction in the magnetic field.

(A. E. R.) Bureau of Standards,
(G. B.) Dept. of Terrestrial Magnetism,
Washington, D.C.,
September 27, 1924.

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* Since in this case there are only two angular variables and three coordinates the system is degenerate unless relativistic mechanics are used. The question as to what happens to the character of the relativistic system in the presence of an electric field simultaneously with the magnetic is not clear.

LIII. *On the Frequency of the Eddies generated by the Motion of Circular Cylinders through a Fluid.* By E. F. Relf, *A.R.C.Sc.*, *and* L. F. G. Simmons, *B.A.*, *A.R.C.Sc.*,* *of the Aerodynamics Department, National Physical Laboratory.*

IN a previous communication † a comparison was made between the frequency of the eddies generated behind a circular cylinder, (i.) as observed directly in a water channel and (ii.) as deduced from the singing of fine wires exposed to a current of air. It was shown that the frequency of the note heard in the second case agreed with the frequency of the eddies formed in the first case, provided that the comparison was made under conditions which were identical according to dimensional theory,—*i. e.*, at the same value of the "Reynolds' number" VD/ν ‡.

The present paper describes measurements of the eddy frequency conducted at higher values of VD/ν ‡. These reveal an interesting connexion between frequency and the drag coefficient, which is clearly shown by the accompanying diagram.

The frequencies measured were in general too low to permit aural determination, and a new method had to be employed. Cylinders of various diameters were placed in a wind-tunnel, extending from wall to wall, and a short platinum wire about 0·001 in. diameter was mounted parallel to the axis of the cylinder, usually about two diameters downstream. The wire was heated by means of an electric current until it was on the point of glowing. In order to measure the frequency of the current charges induced by the eddy motion, a step-up transformer was included in the heating circuit, the secondary of which was connected through suitable resistances to a vibration galvanometer. At each wind speed, the tuning of the galvanometer was adjusted until marked resonance occurred. Under these conditions the natural frequency of the galvanometer coincided with that of the disturbance; the galvanometer was then connected to a single phase alternator, and the speed of rotation of the alternator varied until resonance was again obtained, when an observation of the alternator speed led at once to a determination of the frequency to which the galvanometer had been tuned. The process was repeated at various wind speeds between 20 and 60 ft./sec. with cylinders of 3 in., 9 in., and 1 ft. diameter.

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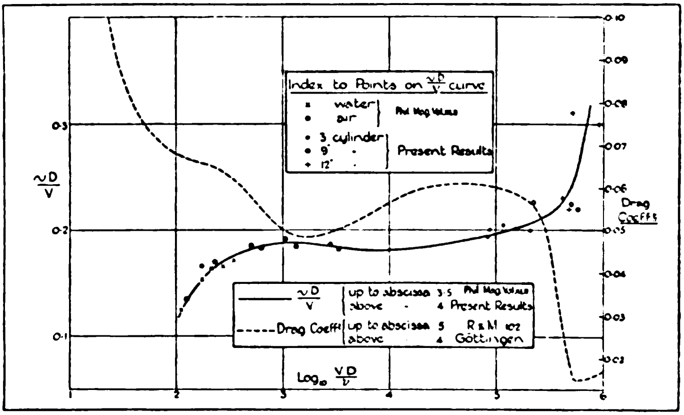
* Communicated by Mr. R. V. Southwell.

† Relf, Phil. Mag. ser. 6, xlii. p. 173 (1921).

‡ V here denotes the free-stream velocity, D the diameter of the cylinder, and ν the kinematic viscosity.

The results obtained from the experiments are shown in the figure, together with corresponding results from the earlier paper cited above, and a curve of drag coefficient*. The ordinates of the full-line curve represent values of $\frac{\sim D}{V}$ plotted against $\log_{10}\frac{VD}{\nu}$, where $\sim$ is the eddy frequency. It will be seen that there is a definite relationship between the curves of frequency and resistance, inasmuch as a reduction in drag coefficient corresponds with a rise in the eddy frequency. This is especially marked in the regions comprised between $\log_{10} VD/\nu = 2$ to 3, and 5 to 6. Below $VD/\nu = 100$ eddy motion does not occur, and in this region it has been shown that † the drag coefficient is calculable with reasonable accuracy from Oseen's approximation to the equations of motion. Between $VD/\nu = 100$ and 1000 the drag coefficient falls, reaching a minimum at about $VD/\nu = 1600$, while the eddy frequency rises to a maximum at about the same value of VD/ν.



The special interest of the present results is in connexion with the rapid fall of drag coefficient in the region between $VD/\nu = 10^5$ and 10^6, which was first observed in experiments at Göttingen ‡ and later confirmed by tests made at the

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[*] The curve of drag coefficient has been taken from tests on the resistance of wires, made at the N. P. L. (Advisory Committee for Aeronautics, R. and M. 102) up to $VD/\nu = 10^4$, and from experiments made at Göttingen (*Phys. Zeits.* 1921, p. 332) for higher values of VD/ν.

[†] Bairstow, Cave, and Lang, Proc. Roy. Soc. A. c. pp. 394–413 (1922).

[‡] *Loc. cit.*

National Physical Laboratory. Measurement of eddy frequency in this region was very difficult, as would be expected from the obviously critical nature of the flow, and no definite periodicity at a given wind speed could be observed. It was, however, possible in all cases to measure the frequencies of the most prominent disturbances present: these figures are plotted in the curve, and there can be no doubt that the frequency rises rapidly at the value of VD/ν where the rapid fall in drag occurs. The precise nature of the change of flow occurring in this region cannot be determined by experiments of the kind here described, and observations by means of smoke would be very difficult, if not impossible, owing to the high wind speed necessary with a cylinder of reasonable diameter. It is considered probable that the general eddy motion filling the whole space behind the cylinder (which has often been observed photographically at lower values of VD/ν) is giving place to a dead-air region which is fringed by smaller eddies. This explanation, though it can at present only be regarded as tentative, seems to account for the rise of eddy frequency observed, and also for the rapid fall of drag coefficient.

So far as the writers were able to determine with the means at their disposal, the flow at values of $VD/\nu < 10^5$ was accurately periodic, whilst above this limit (*i. e.* in the critical region) the flow was definitely aperiodic.

LIV. *On Strain Components in Curvilinear Coordinates.* By A. W. CONWAY, *M.A., D.Sc., F.R.S., University College, Dublin* [*].

THE following method of obtaining the strain components is, perhaps, less difficult than those usually given in treatises on elasticity. Let the square of the line element ds^2 in any system of orthogonal coordinates be given by

$$ds^2 = g_1 dx_1^2 + g_2 dx_2^2 + g_3 dx_3^2.$$

Let the infinitesimal displacements be determined by the changes ϕ_1, ϕ_2, ϕ_3 in the coordinates x_1, x_2, x_3. The *actual* displacements $(u_1, u_2, u_3) = (\surd g_1 \phi_1, \ \surd g_2 \phi_2, \ \surd g_3 \phi_3)$ and the direction cosines

$$(l_1, l_2, l_3) = (\surd g_1 \, dx_1/ds, \ \surd g_2 \, dx_2/ds, \ \surd g_3 \, dx_3/ds).$$

Let (l_1, l_2, l_3) be the direction cosines of a straight line P_0P_1 of any length. Let P_0', P_1' be the extremities of the deformed line and P_0'', P_1'' the projections of P_0', P_1' on $P_0 P_1$. Then for an infinitesimal displacement the increase of length of $P_0 P_1$ is $P_0'' P_1'' - P_0 P_1$ or $P_1 P_1'' - P_0 P_0''$, *i. e.* the difference between the projections along $P_0 P_1$ of the displacements of P_0 P_1 or

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[*] Communicated by the Author.

$$\left[g_1\phi_1\frac{dx_1}{ds}+g_2\phi_2\frac{dx_2}{ds}+g_3\phi_3\frac{dx_3}{ds}\right]_0^1.$$

Hence if $P_0 P_1$ is a line element we get for the elongation along $P_0 P_1$

$$\frac{d}{ds}\Sigma\left(g_r\phi_r\frac{dx_r}{ds}\right)\quad(r=1,2,3).$$

Here we can shorten the expressions by introducing the "dummy" notation of tensor algebra. We have then

$$\frac{d}{ds}\left(g_r\phi_r\frac{dx_r}{ds}\right)=\phi_r\frac{d}{ds}\left(g_r\frac{dx_r}{ds}\right)+g_r\frac{dx_r}{ds}\frac{d\phi_r}{ds}$$

$$=\phi_r\frac{d}{ds}\left(g_r\frac{dx_r}{ds}\right)+g_r\frac{dx_r}{ds}\frac{dx_i}{ds}\frac{\partial\phi_r}{\partial x_i}.$$

The first expression can be transformed by means of the differential equations of a straight line in the coordinates x_1, x_2, x_3. These of course can be obtained from the equation $\delta\int ds=0$ or from the dynamical analogue as follows.

Let a particle of unit mass move along $P_0 P_1$ with uniform unit velocity, then $dt=ds$ and the kinetic energy is

$$\tfrac{1}{2}g_r\left(\frac{dx_r}{ds}\right)^2.$$

Expressing by Lagrange's method that the generalized forces are zero, we get

$$\frac{d}{ds}\left(g_1\frac{dx_1}{ds}\right)=\tfrac{1}{2}\left(\frac{dx_i}{ds}\right)^2\frac{\partial g_i}{\partial x_1}$$

and two similar equations. Inserting in the above relation we get finally for the elongation

$$g_r\frac{dx_r}{ds}\frac{dx_i}{ds}\frac{\partial\phi_r}{\partial x_i}+\tfrac{1}{2}\phi_r\frac{\partial g_i}{\partial x_r}\left(\frac{\partial x_i}{\partial s}\right)^2.$$

Inserting the values of (l_1, l_2, l_3) and (u_1, u_2, u_3) we then obtain the usual expressions. It is of course obvious that the method applies exactly in a similar way to non-orthogonal coordinates.

LV. "*Semi-optical*" *Lines in the X-ray Spectra.*
By E. BÄCKLIN, M. SIEGBAHN, *and* R. THORÆUS *.

THE nowadays existing detailed systematization of the X-ray spectra is based upon the assumptions of Kossel, that the X-ray lines are emitted on transitions of electrons between orbits which are normally occupied by electrons. In reality it has been supposed that a certain spectral line disappears at the same time as the electronic shell from which the electron starts, and in general the experiments seem to support this view. Thus we are able to define the true X-ray spectral lines as transitions between energy levels which are normally occupied by electrons. Complementary to this the optical spectral lines belong to transitions from a free outer orbit to a vacant place in the outmost energy shell.

In connexion with some investigations made by Thoræus and Siegbahn † to extend the range of registered wave-lengths within the K-series and some peculiarities found by Mr. Bäcklin in the $K\beta_1$ line of the elements Mg (12) and Na (11), we have performed a particular investigation in order to clear up this point.

In the investigation mentioned above the K-series of F (9) has been studied. Although the $K\alpha$ line ($\lambda = 18{\cdot}37$ Å.U.) was very strong, no trace of the $K\beta_1$ line was to be seen on the photographic plate. This is quite in agreement with the above criterion on X-ray lines, as the $K\beta_1$ line belongs to a transition from an M-orbit to the K-shell. At F (9), however, the M-shell is unoccupied, and so the $K\beta_1$ line cannot be expected. There is no doubt that Na (11) is the last element where the M-level is normally occupied by at least one electron. From Na (11) upwards the $K\beta_1$ line has been registered and measured, but it may be mentioned that this line is relatively very weak at Na (11), at least in comparison with that one of Al (13). When plotting the wave-length difference $K\alpha - K\beta_1$ against the atomic number Z as in fig. 1 *b*, we get a curve of surprising appearance. The peculiarity of this curve is surely due to the $K\beta_1$ line and shows that this line behaves quite regularly down to Al (13) but is singular at Mg (12) and Na (11).

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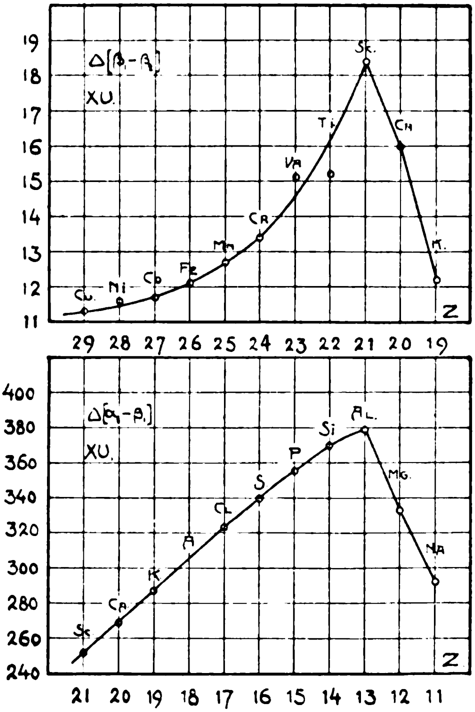
* Communicated by the Authors.

† Read before the Royal Swedish Academy of Science, Nov. 26th, 1924, and will appear in *Arkiv f. Mat., Astr. o. Fys.*

Fig. 1 *a*, *b*.



The same phenomenon may also be seen directly on the scheme (fig. 2) of all the K-lines of the elements Na (11) to Sc (21). Here the spectra are arranged one above the other in such a way that the Kα lines are on the same vertical. All the lines excepting α and β_1 are spark lines, which are very common in this region. The irregular displacement of the β_1 line at the last two elements Mg (12) and Na (11) is evidently to be seen.

This peculiarity may be considered in the light of the scheme of the atomic model recently given by Stoner * compared with the systematization of the X-ray spectra. Fig. 3 gives a diagram of the energy levels at Na (11), where 5 (1K, 3L and 1M) are normally occupied by electrons and constitute the X-ray levels. Beneath them the free orbits as given by the ordinary arc spectrum are drawn. Of the 11 electrons, 2 belong to the K-, 8 to the L- and 1 to the first M-level. Now Stoner has put forward the idea, that the 8 electrons of the L-level are distributed as shown in fig. 3, that means 2 in the L_I, 2 in the L_{II}, and 4 in the L_{III}. The 11th electron is then placed in the M_I.

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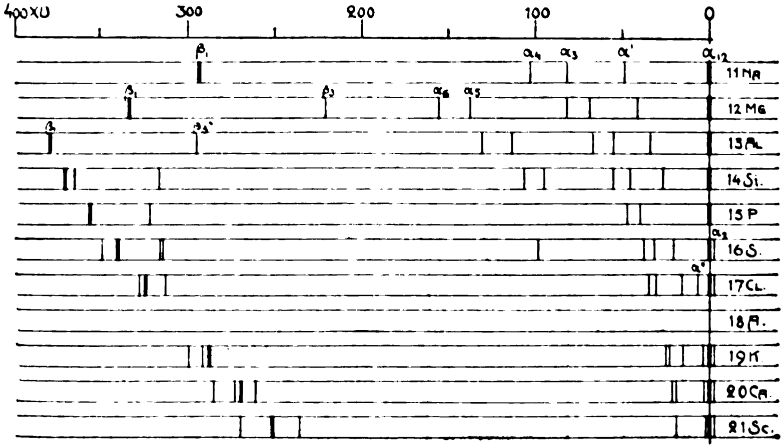
* Phil. Mag. ser. 6, xlviii. No. 286, Oct. 1924.

Fig. 2.

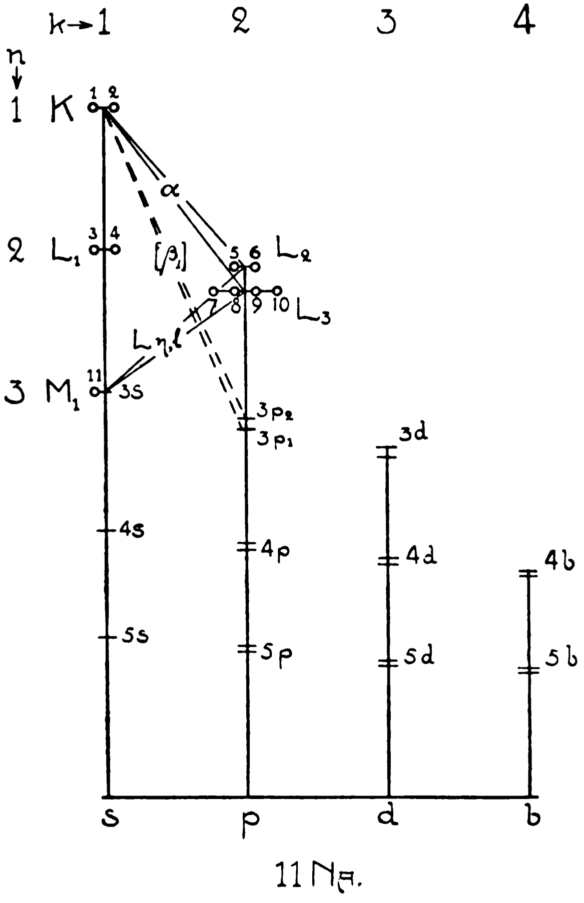


Consequently the β_1 line should not exist as a true X-ray line in the K-spectrum of Na (11). The same should occur at the next element Mg (12), where there are 2 electrons in the M_I-shell. At first at Al (13) the M_{II}-shell gets one electron, and from this element upwards the true $K\beta_1$ line should appear.

The above is supported by the curve in fig. 1, which shows that the line called $K\beta_1$ is not a direct continuation of the $K\beta_1$ of the higher elements. It might be considered as a "semi-optical" line which is emitted by an electron starting from a free level of the atom, or say a true X-ray line belonging to a metastable form of the elements where the outmost electron is moving in another orbit than that one of the normal atom.

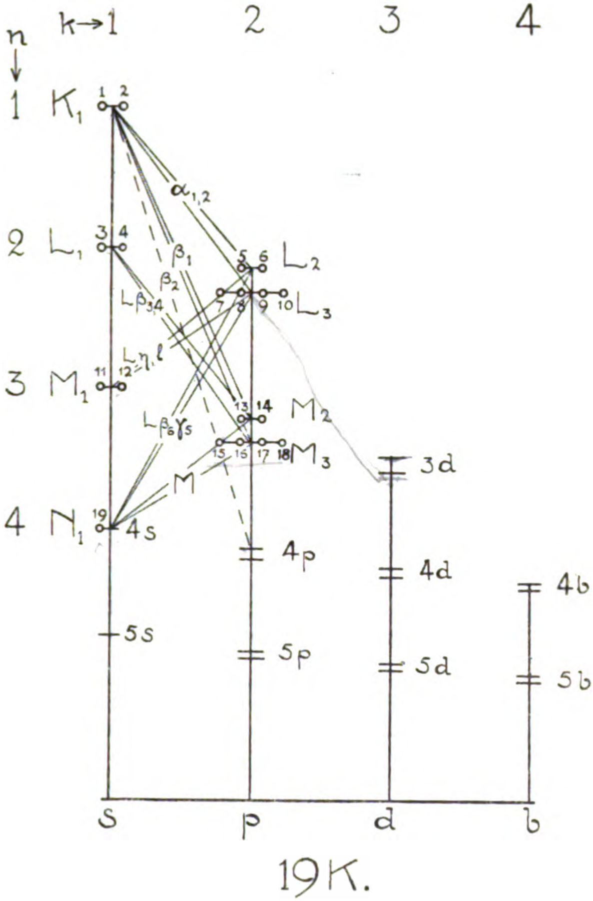
Quite the same phenomenon as at Na (11) may also be shown to occur at K (19) where the electronic arrangement is similar to that of Na. But in this case the peculiarity is to be expected in the $K\beta_2$ line, as may be seen from fig. 4. When plotting the wave-length difference $K\beta_1 - K\beta_2$ against the atomic number Z we get a curve fig. 1 *a*, which has the same general appearance down to K (19) as that one of $K\alpha - K\beta_1$ at the elements next to Na (11). The line called β_2 of the two elements Ca (20) and K (19) is displaced against longer wave-lengths.

Fig. 3.



Similar irregularities of the X-ray lines in the neighbourhood of the last element, where the line in question disappears, are also to be found in some other cases. Due to the more complicated structure and building-up process of the higher elements, however, the interpretation is here not as simple as in the two cases discussed above..

Fig. 4.



Upsala, Physical Laboratory.
Dec. 3rd, 1924.

LVI. *Gas Ion Mobilities.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN an article of mine in your Journal, I derived an expression for ionic mobilities based on a recent theory of J. J. Thomson and a classical equation due to Langevin. In analysing the derivation of Langevin's equation, it appeared that what he calls λ in his equation is $\frac{1}{\pi\sigma^2 N}$, and not, as has been supposed, the quantity $\frac{1}{\pi\sqrt{2}\sigma^2 N}$, containing the correction term for Maxwell's distribution of velocities. Thus the ionic mobility equation which I published, giving the mobility in cm./sec. volt/cm. should be multiplied by $\sqrt{2}$, as should also the resulting values of the computed mobility. The equation given was:

$$K = \frac{0{\cdot}0735\sqrt{\frac{1+b}{b}}}{\frac{p}{760}\sqrt{(D-1)M_0}} \text{ cm./sec. per volt/cm.}$$

It should be

$$K = \frac{0{\cdot}104\sqrt{\frac{1+b}{b}}}{\frac{p}{760}\sqrt{(D-1)M_0}} \text{ cm./sec. per volt/cm.}$$

The computed mobilities in the table then become :—

Gas.	Comp.	Obs.	Gas.	Comp.	Obs.
H_2	6·27	6·02	SO_2	·20	·44
He	8·50	5·09	N_2O	·68	·82
A	2·32	1·37	C_2H_5OH ...	·23	·34
Air	1·12	1·35–1·6	CCl_4	·18	·30
NH_3	·41	·74– ·52	C_2H_5Cl	·14	·33
CO_2	·72	·81	$C_4H_{10}O$	·20	·24
CO	1·04	1·10			

These, it is seen, in general agree with the observed values more closely than before.

In a footnote on p. 448 a doubt was cast on the legitimacy of the introduction of the Thomson factor into the Langevin mobility equation, and the desirability of a rigorous derivation of the Langevin equation assuming attractive forces was indicated. The writer has since discovered a paper by Langevin in the *Annales de Chimie et de Physique*, viii. 5, p. 238 (1905), in which he makes such a rigorous derivation, starting from a somewhat different viewpoint. The resulting equation for the case of an inverse fifth-power law written in the writer's notation is

$$K = \frac{0{\cdot}235\sqrt{\frac{M+m}{m}}}{\sqrt{\frac{p}{760}(D-1)M_0}}.$$

As is seen, this is identical with the writer's equation except for a numerical factor of 0·235 instead of ·104, and except for the fact that it contains $\sqrt{\frac{p}{760}}$ instead of $\frac{p}{760}$, The latter difference may be due to a numerical blunder in Langevin's treatment of the constants.

This beautiful piece of analysis therefore completely confirms in its general outlines the conclusions arrived at by the writer, and indicates that in an equation of this type there lies the proper solution of the ionic mobility problem. It is only to be regretted that the lack of experimental development of this field of work at the time of Langevin's paper did not enable him to see its full importance, and thus permit him to give this brilliant piece of work all the publicity it deserved.

Leonard B. Loeb.

Department of Physics,
University of California,
Berkeley, California,
October 11, 1924.

LVII. *Notices respecting New Books.*

John William Strutt, Third Baron Rayleigh, O.M., F.R.S. By his son Robert John Strutt, Fourth Baron Rayleigh, F.R.S. (London: Edward Arnold & Co., 1924.)

It is a matter of very great satisfaction to Mathematical Physicists, and indeed to scientific men and women generally, to welcome the interesting and vivid account of the great Lord Rayleigh contained in this book, The work of Rayleigh will continue to be of very great importance until the present generation of scientists is long since passed, and the record of his intellectual life and of the activities of his mind are, fortunately, safely preserved for posterity in the 446 papers in the six large volumes of his collected writings. But the memory of Rayleigh as a great figure of a man, would necessarily fade, as those who knew him in turn leave their scientific labours to the next generation. The present Lord Rayleigh, in putting on paper all the many sides of his distinguished father, has earned our gratitude, and we value this record of Rayleigh as a human being, and place it beside his collected works with great satisfaction.

It is unnecessary to give any detailed account of the contents of the book. The varied interests of Rayleigh will make the interesting expositions by the author appeal to almost every scientist, and the account of Rayleigh's every-day life makes an interesting and vivid picture of a great Victorian.

A History of British Earthquakes. By Charles Davison, Sc.D., F.G.S. (Cambridge University Series. 1924.)

By this valuable History and compilation Mr. Davison adds substantially to the services he has already rendered to seismological science. The 'History of British Earthquakes' will save from oblivion and render available many hundreds of valuable records of earthquakes in Britain.

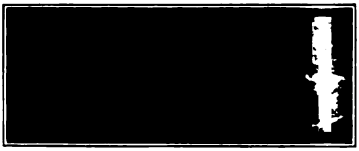
It is, indeed, an astonishing record. We find no less than 1191 well attested earthquake shocks recorded in the British Isles since the year 974 A.D. Mr. Davison's analysis of these seismic records shows--as might be expected—that repetitional shocks in certain faulted areas account for the greater number of these earthquakes. Thus the Great Glen fault and the Highland Border fault have been specially productive: the latter giving rise to the very large number of closely localized seismic disturbances of the Comrie district. There appears no reason to question the view taken by Mr. Davison that British earthquakes are, in nearly every case, associated with slowly progressing fault-movements. In Mr. Davison's map showing the distribution of British earthquakes we find that the seismic areas are numerous and widely distributed. The author estimates that about half the area of Great Britain has at different historic times been affected by seismic disturbances. He draws attention to the comparative freedom of Ireland from such disturbances.

The question of periodicity is one of great interest, but the analysis of the distribution in time of British earthquakes, although leading to an apparent diurnal periodicity, appears far from decisive. The periodicity may be apparent only, and due—as Mr. Davison suggests—to more favourable conditions for observation recurring at particular times of the day. More definite are conclusions respecting the westerly migration of foci. This phenomenon appears to be frequently exhibited, the stability of the Comrie foci being an interesting exception. Mr. Davison's discussion of twin earthquakes is a good instance of the valuable contributions to seismology which he is able to extract from his great compilation. His already published theory ('Manual of Seismology,' 1921) of the origin of such earthquakes as due to the growth of a crust-fold the axis of which is cut by a fault-plane, appears to be the best explanation so far offered of the occurrence of nearly simultaneous shocks emanating from foci separated by a few miles of inter-focal region.

One lesson of special importance should be learned from these and similar records: the fact of the *constant* yielding of the earth's continental crust to comparatively feeble stresses. We should expect this on *à priori* grounds. For regionally disturbed and faulted rocks will not behave the same as a small hand specimen of flawless rock placed in a hydraulic press. It is sometimes assumed, however, that they will; and upon this assumption a theory of the cyclical development of mountain chains as arising out of an assumed slowly and uniformly cooling and shrinking Earth and the accumulation of strain upon an enormous scale, is based. The seismic phenomena apparent all over the Globe, and emanating from various depths in the crust, demonstrate that such great strains cannot and do not accumulate. J. J.

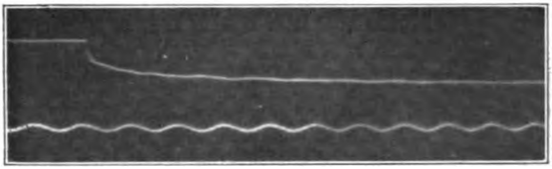
[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

FIG. 8.



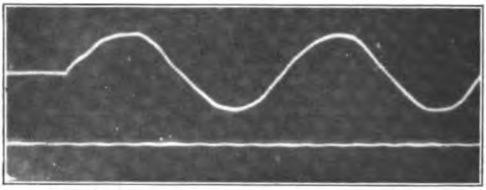
Sudden application of potential--no damping.

FIG. 9.



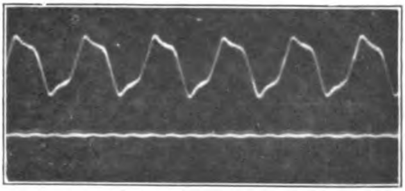
Sudden application of potential—artificial damping.

FIG. 10.



Terminal voltage of rotary converter. 50~, 260 volts.

FIG. 11.

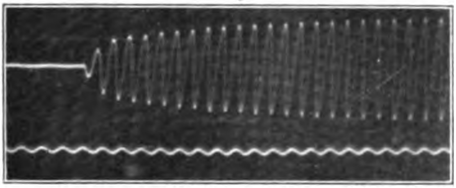


Secondary voltage of transformer, supplied by inductor alternator. 100~, 210 volts.

Fig. 12.

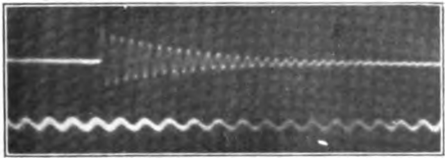
Terminal voltage of high-frequency alternator.
700 ~, 240 volts.

Fig. 13.



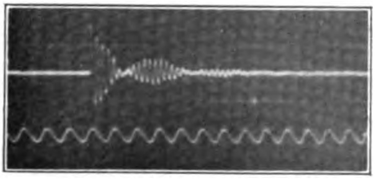
Valve oscillation, frequency 485.

Fig. 14.

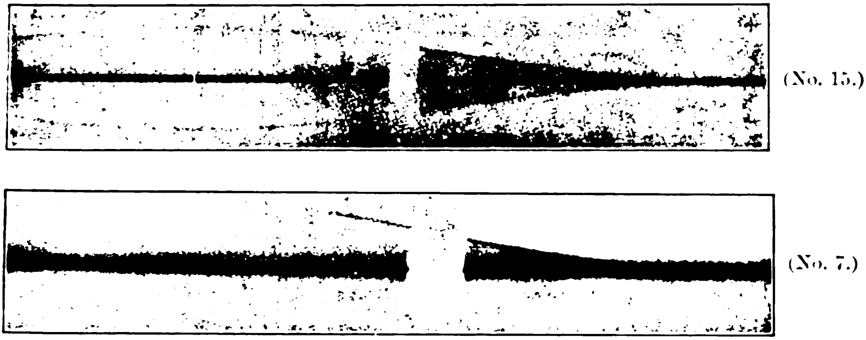


Oscillatory discharge of condenser.

Fig. 15.



Oscillatory discharge of condenser in a coupled circuit.



A. H. Bucherer.

Fig. 1. (Taken from the *Annalen der Physik*. IV. vol. xxviii., 1909).

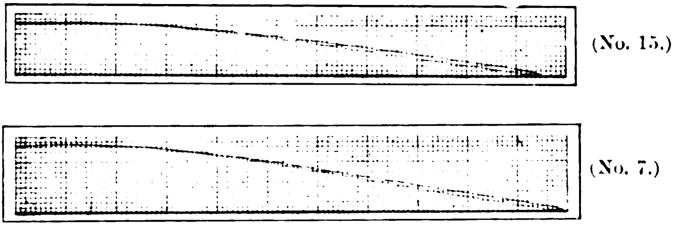


Fig. 2.

Full line —— for Einstein's curve; dotted line - - - - for Doi's curve.

Fig. 3. (For Experiment No. 15).
The middle point between the two vanishing ends lies at about 3 mm. to the left of the original mark on the zero-line.

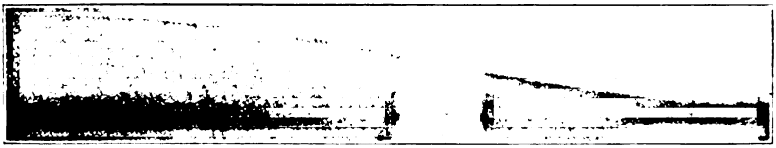


Fig. 4. (For Experiment No. 7).
Not the centre-line, but the upper margin, of the broad undeflected trace is to be regarded as the zero-line with Bucherer's value $z_{max.} = 1·35$ mm.

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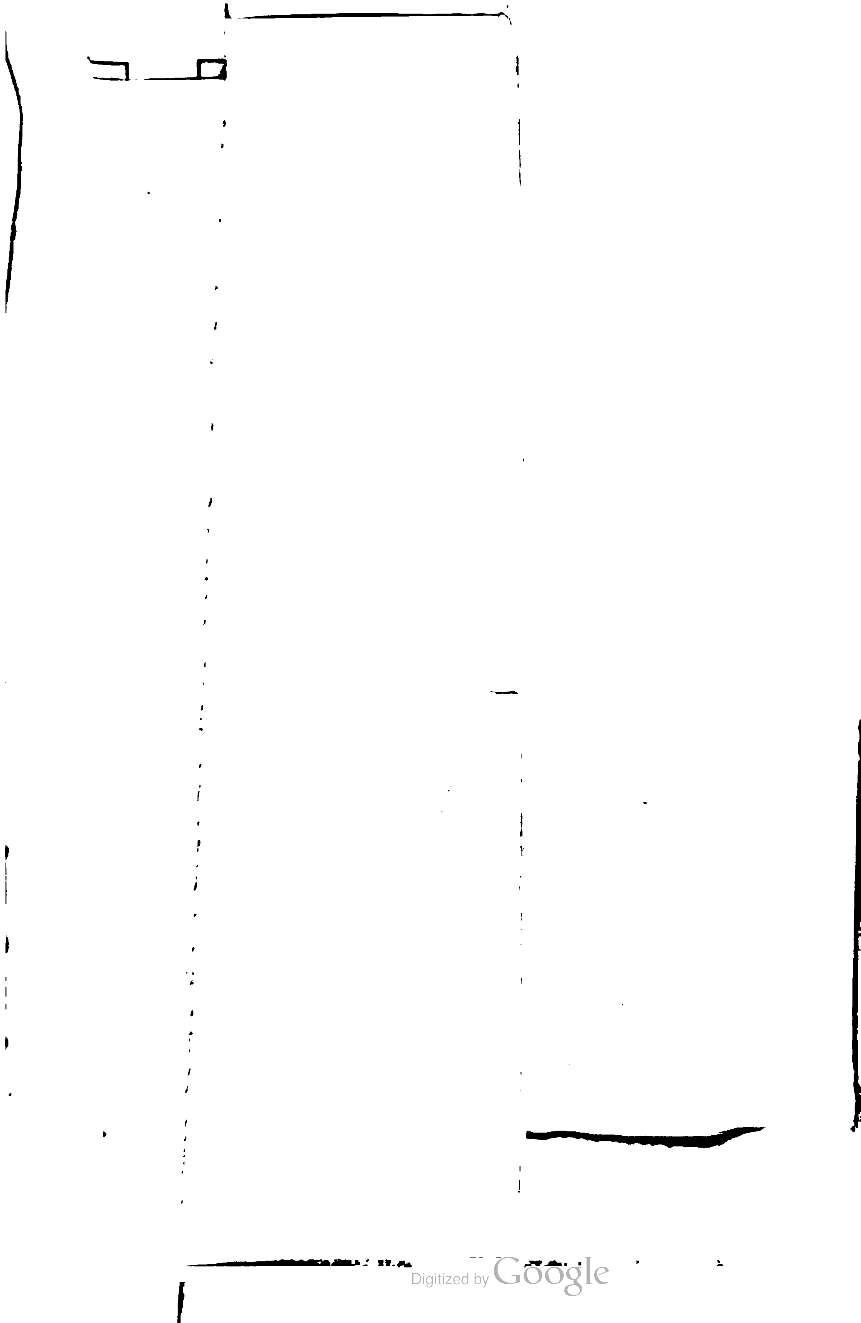
IG. 11.



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[SIXTH SERIES.]

MARCH 1925.

LVIII. *On the L-absorption Spectra of the Elements from* Sn (50) *to* W (74) *and their Relation to the Atomic Constitution. By* Y. NISHINA, *Physicist, the Institute of Physical and Chemical Research, Tokio* *.

[Plate VIII.]

Introduction and Summary of Results.

BOHR and Coster emphasized † the characteristic features displayed by Moseley's curves in those parts of the natural system where, according to Bohr's theory, the completion of inner groups of electrons in the atoms is in progress, *i. e.* in the neighbourhood of iron-, palladium-, and platinum-groups as well as the rare earths. In a paper by Coster, Werner, and the present writer ‡, the result of the measurements of the L-absorption spectra of nine elements between La (57) and Hf (72) was given. These measurements agreed well with the interpolated values which were used by Bohr and Coster in their paper. In view of the importance of more accurate values of the energy levels free from the uncertainty involved in the interpolation and arising from the lack of uniformity of the measurements of different authors, the present writer has undertaken the further measurements of X-ray absorption spectra in general. This paper gives a part of the result of measurements which are still in progress, and it forms the continuation of the work mentioned above*. The results of these measurements enable us to give more exact values of the different energy levels for the elements from Sn (50) to W (74).

---

* Communicated by Prof. N. Bohr.

† *Zs. für Phys.* xii. p. 342 (1923).

‡ *Zs. für Phys.* xviii. p. 207 (1923).

A plotting of the square roots of the level values as a function of the atomic number confirms in a striking way the general conclusions of Bohr and Coster. Especially do these curves allow us to trace with considerable certainty the beginning and the end of the gradual development of the group-structure of the atom which takes place within the family of the rare earths. The closer discussion brings some further problems to light, for which, however, neither the theory nor the experiment at present allows of definite conclusions.

Experimental Arrangement and Results.

The apparatus used and its arrangement are the same as mentioned in our previous work †. The vacuum spectrograph and metal X-ray tube of Prof. Siegbahn provided with a mercury vapour pump constitute the main parts. The radius of this spectrograph is 121·4 mm. The source of energy is a transformer of 30,000 volts with a kenotron rectifier (hot cathode rectifier).

The absorption screen is prepared by rubbing the finely-powdered chemical compounds of the elements under examination on a thin sheet of silk paper. As mentioned by Fricke ‡, Lindh §, and also by us in the previous work ‖, the thickness of the material on the screen plays an essential part in obtaining the detailed structure of the absorption spectra. With the thickness of the screen varying from 1 mg. to 7 mg. per sq. cm. of each element, good results were obtained. In order to get good L_{I}-absorption spectra, which are extremely weak and diffuse in comparison with the L_{III} and L_{II}, a thicker screen is to be used. The screen was placed between the slit and the crystal.

The samples of the rare earths used in the experiment were all presented to this Institute by Freiherr Auer von Welsbach, whose kindness enabled this work to be completed.

---

[*] Coster, Nishina, and Werner, *loc. cit.*

[†] *Loc. cit.*

[‡] Phys. Rev. xvi. p. 202 (1920).

[§] Dissertation Lund (1923).

[‖] *Loc. cit.*

The elements which were investigated were in the form of the following compounds:—

74 WO_3, 73 Ta_2O_5, 72 HfO_2, 67 $Ho_2(SO_4)_3$+aq., 65 Tb_2O_3, 64 $Gd_2(SO_4)_3$+aq., 63 $Eu_2(SO_4)_3$+aq., 62 $Sm_2(SO_4)_2$+aq., 60 $Nd_2(SO_4)_3$+aq., 59 $Pr_2(SO_4)_3$+aq., 56 $BaSO_4$, 55 CsCl, 50 SnO_2.

In order to get strong continuous radiation a tungsten anticathode was used. After the exposure for absorption spectra, the duration of which ranged from 2 to 15 hours, the exposure for emission lines of reference was generally necessary. For this purpose the tungsten anticathode is replaced by a copper one having the necessary compound on it, which is then exposed for ¼ to ½ hour. In case of TaL_I, YbL_{II}, TbL_I, and GdL_I the emission lines $L\gamma_3$, $L\beta_2$, $L\eta$, and $L\alpha_1$ respectively of tungsten come quite near the absorption edges in question, thus excluding the use of a tungsten anticathode. Generally the hot cathode of the X-ray tube is also of tungsten wire, and in that case some tungsten lines due to a deposit of tungsten on the anticathode cannot be avoided. In order to get rid of these difficulties, tantalum or molybdenum wire, both of which were put at our disposal by the kindness of Prof. Pirani, Studien-Gesellschaft für elektrische Beleuchtung in Berlin, was used for the hot cathode, and the following metals were used as the anticathode:—

For TaL_I, Pt. For TbL_I, Au.
„ YbL_{II}, Au. „ GdL_I, Pt.

The tantalum and molybdenum wires, however, burn out in a much shorter time than the tungsten wire, thus making the experiment more troublesome.

The voltage used was never more than twice the critical tension for the absorption spectrum in question. This limitation of voltage prevents the second-order continuous spectrum which is not absorbed by the screen from overlapping and masking the absorption spectrum under examination. The current through the X-ray tube ranged from 8 to 20 milliamperes, according to the metal of the anticathode used. Too much current should be avoided as it results in making a deep hole in the anticathode when the focussing is sharp, and the radiation in the direction of the slit is thereby stopped.

During the exposure the crystal was turned automatically and uniformly to and fro through about one degree in order to get homogeneous exposure on both sides of the absorption edge. Calcite was used as the crystal for all elements except tungsten, for which rock-salt was used.

The method of measurement of the plate is the same as in our previous work[*]. As will be explained later, the absorption edge appears on the plate as a white line. The distance between the middle of this white line and the middle of the reference emission line is measured by means of Hilger's micrometer. Usually one or two emission lines, each on both sides of the absorption line, are used for reference, and the mean value of the glancing angle obtained from these measurements is used for the calculation of wave-length and frequency.

The results of the measurements are given in Tables I., II., and III. The accuracy of the measurements is about the same as that of our previous work. Usually the error of the measurements of the distance between the absorption line and the reference emission line on the plate is smaller than 0·03 mm. which corresponds to less than 0·7 X.U. in the wave-length. This makes an error in the frequency of 0·1 unit in the case of $\mathrm{SnL_{III}}$ and about 0·7 unit in the case of $\mathrm{WL_{I}}$. The error in the $\mathrm{L_{III}}$ edge is usually less than this, and in the case of the edges whose figures are given up to the second decimal in the frequency in Table III., the error is less than half the value mentioned.

Table I.—$\mathrm{L_{I}}$.

Element.	Glancing angle.	λ.	ν/R.	ν/R interpolated or measured before.
74 W	10° 26·8′ (rock-salt)	1020·5	893·0	890·6
73 Ta	10 2·9 (calcite)	1057	862	860·3
72 Hf	10 25·0 ,,	1095·3	832·0	
67 Ho	12 32·0 ,,	1314·6	693·2	692·9
65 Tb	13 32·3 ,,	1418·1	642·6	642·4
64 Gd	14 4·9 ,,	1474·0	618·2	617·4
63 Eu	14 39·6 ,,	1533·3	594·3	593·6
62 Sm	15 16·2 ,,	1595·4	571·2	570·7
60 Nd	16 36·6 ,,	1731·7	526·2	525·8
59 Pr	17 21·3 ,,	1807·1	504·3	504·2
56 Ba	19 54·0 ,,	2062·0	441·9	442·3
50 Sn	27 10·4 ,,	2766·7	329·4	—

---

[*] *Loc. cit.*

TABLE II.—L_{II}.

Element.	Glancing angle.	λ.	ν/R.	ν/R interpolated or measured before.
74 W	10° 58·4′ (rock-salt)	1071·3	850·6	850·1
73 Ta	10 33·6 (calcite)	1110·2	820·8	821·0
70 Yb	11 48·2 ,,	1239·2	735·4	735·7
67 Ho	13 14·0 ,,	1386·9	657·1	657·4
65 Tb	14 19·0 ,,	1498·1	608·3	608·2
63 Eu	15 32·3 ,,	1622·8	561·5	561·3
62 Sm	16 12·6 ,,	1699·1	538·9	539·0
60 Nd	17 40·3 ,,	1839·1	495·5	495·9
59 Pr	18 28·7 ,,	1920·1	474·6	474·7
56 Ba	21 17·2 ,,	2199·3	414·3	414·7
55 Cs	22 23·4 ,,	2307·5	394·9	395·0

TABLE III.—L_{III}.

Element.	Glancing angle.	λ.	ν/R.	ν/R interpolated or measured before.
74 W	12° 25·9′ (rock-salt)	1211·6	752·1	751·6
73 Ta	11 55·4 (calcite)	1251·7	728·0	728·6
67 Ho	14 39·0 ,,	1532·2	594·7	595·0
65 Tb	15 45·5 ,,	1645·3	553·9	553·8
63 Eu	17 0·3 ,,	1771·7	514·4	514·1
62 Sm	17 41·4 ,,	1840·8	495·0	495·0
60 Nd	19 11·0 ,,	1990·7	457·76	457·9
59 Pr	20 0·5 ,,	2072·8	439·63	439·4
56 Ba	22 53·6 ,,	2356·8	386·66	386·7
55 Cs	24 2·1 ,,	2467·4	369·32	369·5
50 Sn	31 18·0 ,,	3147·3	289·54	—

Of course, all the errors in the determination of the grating constant of the crystal and the measurements of the wave-length of reference lines come in our results, but we expect these to be very small compared with the error mentioned above.

In the last column of the tables the values given by Bohr and Coster in the above-mentioned work are quoted. Except in the case of L_I, the discrepancies with the measured values lie within the limit of the experimental error in most elements. In case of L_I, on the other hand, there exists the same kind of systematic difference of less than 1 unit in frequency in the direction of higher values as was found in our previous measurements, except for W and La, where the difference is very large. In case of TaL_I there exists some doubt as to the identification of the absorption line, because we should expect Pt$L_{\beta_{10}}$ quite near the absorption line in question, and, in fact, the absorption line on the plate seemed sharper on the longer wave-length edge than is usually the case with the L_I-lines. Thus it may be possible that the longer wave-length side of the absorption line is overlapped by $PtL_{\beta_{10}}$. Consequently we should reserve the conclusion as regards the real existence of the rather large difference between the measured value and the interpolated one as shown in the table.

As is well known now, the structure of the absorption spectra is not simple. If the thickness of the absorbing screen is suitably prepared, the X-ray absorption spectra appear on the photographic plate as white lines instead of absorption edges, as was formerly accepted. In some cases, not only the one white line which is measured and given in the above tables, but a second or even a third white line is observed, one closely following the other on the shorter wave-length side of the main absorption line. The general details of such fine structure displayed on the plates which were obtained with the compounds used in this experiment will be described here. We shall take the case of HoL_{III}, and follow the plate from the longer wave-length side to the shorter one. At first we see very dark ground showing nearly unabsorbed incident continuous radiation. Then comes the first very strong and sharp white line, which has about the same width as that of the slit, *i. e.* about 0·1 mm. in our case. This white line is followed by a dark band of the width of about 0·2 mm., the intensity of darkness being usually less than the darkness on the longer wave-length side of the first white line. After this dark band follows again a white line, which is much weaker, broader, and more diffuse than the first one, its width being about 0·13 mm. After passing this second white line, we meet either with the dark ground or a second dark band, according to different elements. In the former case the continuous darkness extends on the shorter wave-length side all over the rest of the plate, the intensity of darkness being usually less than that on the longer wave-length side of the first white line. In the latter case the second dark band, which is broader than the first one—for example, 0·3 mm. wide in case of HoL_{III}—is followed by a third white line, which is much broader, weaker, and more diffuse than the second one. After this white line there follows continuous darkness all over the rest of the plate as in the former case. Whether the difference of these two cases lies in the nature of the phenomena or in the difference of the thickness of the absorbing screen or of the conditions of the experiment, and whether more than three white lines exist or not, remains still to be decided. Fig. 1 *a* (Pl. VIII.) is the reproduction of the HoL$_{III}$ spectra and fig. 1 *b* is its photometric curve. They show one example of the latter case. Figs. 2 *a* (Pl. VIII.) and 2 *b*, which are the corresponding reproduction of the SmL$_{III}$ spectra and its photometric curve, show, on the other hand, one example of the former case. It seems to the writer that with a thinner absorbing screen the absorption spectra of the former type is obtained, whereas with a thicker one that of the latter type is obtained.

Fig. 1 *b*.

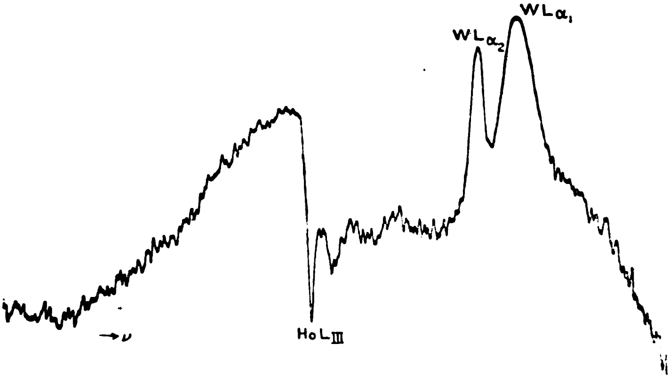
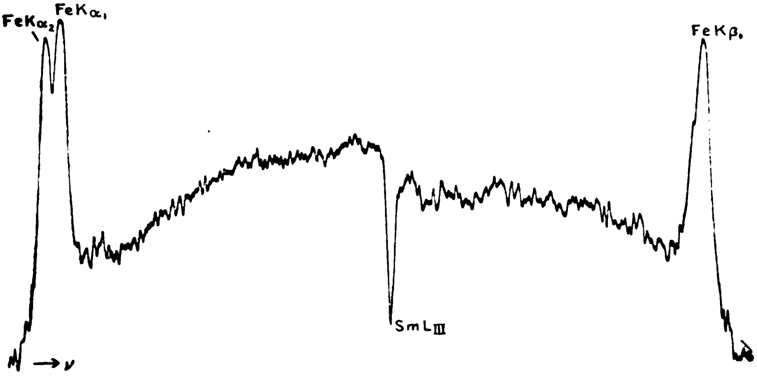


Fig. 2 *b*.



The above description of the fine structure applies generally for the L$_{III}$-absorption spectra. In the cases of L$_{I}$ and L$_{II}$ such detailed structure is very rarely observed. They show usually only the first white line, especially with L$_{I}$, no plate with a second white line having been observed. The first white line in case of L_I, moreover, is very weak, diffuse, and broader than the width of the slit.

TABLE IV.

The second white line lying on the shorter wave-length side of the first L_{III} white line.

	λ.	ν/R.	Δλ.	Δν/R.	ΔV.
67 Ho.........	1525·7	597·3	6·5	2·6	34
66 Dy.........	1580·1	576·7	6·9	2·5	34
63 Eu.........	1763·1	516·9	8·5	2·5	34
62 Sm.........	1831·7	497·5	9·1	2·5	33
60 Nd.........	1980·6	460·1	10·1	2·3	32
59 Pr	2061·9	442·0	10·9	2·4	32

Table IV. gives the wave-length and frequency of the middle of the second white lines, which lie on the shorter wave-length side of the first white line in the case of L_{III}-absorption spectra for different elements. In the third and fourth columns of the table the corresponding differences of the wave-length and the frequency from those of the L_{III}-line are given respectively, the corresponding difference expressed in volts by means of Einstein's formula $eV = h\nu$ being added in the last column. As will be seen, Δλ decreases systematically with the atomic number, the corresponding $\Delta\nu/R$ and ΔV being nearly constant. Here the accuracy of the measurement is not high owing to the

TABLE V.

The third white line lying on the shorter wave-length side of the second L_{III} white line.

	λ.	ν/R.	Δλ.	Δν/R.	ΔV.
67 Ho.........	1515	601·3	17	6·6	89

weakness of the line. The error will be about twice as large as that of the L_{III}-line. In the case of Ho, the wave-length and the frequency of the middle of the third white line lying on the shorter wave-length side of L_{III} could be roughly measured. Their values and their differences from those of L_{III} are given in Table V. On some other plates we can see the third white lines of the same sort, but they are too weak to be measured.

Table VI.

Emission lines.	Glancing angles. Calcite.	λ.	ν/R.	$\sqrt{\nu/R}$.
72 Hf L_{β_7}	12° 24·9'	1302·5	699·7	26·451
Hf L_{β_9}	12 16·0	1287·0	708·1	26·609
Hf $L_{\beta_{5,10}}$	12 20·6	1296·7	703·7	26·527
63 Eu L_{γ_4}	14 44·0	1540·7	591·5	24·320
58 Ce L_l	28 26·8	2885·7	315·79	17·771
55 Cs L_l	32 33·1	3259·6	279·57	16·720
53 I L_l	35 52·2	3549·7	256·72	16·022
I L_{β_4}	28 39·8	2905·9	313·60	17·709
I L_{β_6}	27 51·3	2830·5	321·95	17·943
I L_{β_3}	28 15·5	2868·2	317·72	17·825
I $L_{\gamma_{2\cdot3}}$	23 46·3	2442·1	373·16	19·317
I L_{γ_4}	23 11·8	2386·2	381·89	19·542

Table VI. gives the result of the measurements of some emission lines which have not been measured accurately and are necessary for the calculation of the energy values of other levels in the next paragraph. The accuracy of these measurements is about the same as in the case of the absorption edges mentioned above, since most of these emission lines are weak and diffuse.

The Values of the Energy Levels.

According to Coster's scheme, the results of our previous work and the present one enable us to calculate the values of different energy levels of different atoms by means of the frequency values of emission lines. In doing this, the values given by the following experimental results were consulted:—

L-Absorption ...	74 W–50 Sn, Coster, Nishina, and Werner, *Zs. für Phys.* xviii. p. 207 (1923), and the present measurements.
	53 I–50 Sn, Coster *Zs. für Phys.* xxv. p. 83 (1924).
	56 Ba–51 Sb, Lindsay, *C. R.* clxxv. p. 150 (1922).
L-Emission lines	74 W, Siegbahn, *Phys. Zs.* xx. p. 533 (1919).
	73 Ta, Coster, *Zs. für Phys.* vi. p. 186 (1921).
	72 Hf, 69 Tm, Coster, Phil. Mag. xlvi. p. 956 (1923).
	71 Cp–57 La, Coster, *ibid.* xliv. p. 546 (1922).
	56 Ba–50 Sn, Coster, *ibid.* xliii. p. 1070 (1922).
M-Emission lines	74 W–66 Dy, Hjalmar, *Zs. für Phys.* xv. p. 65 (1923).
	92 U–66 Dy, Stenström, Dissertation Lund (1919).
	74 W, Thoræus, *Zs. für Phys.* xxvi. p. 396 (1924).

TABLE VII.

The Values of Energy Levels (T/R).

	L_I.	L_{II}.	L_{III}.	M_I.	M_{II}.	M_{III}.	M_{IV}.	M_V.	N_I.	N_{II}.	N_{III}.	N_{IV}.	N_V.	N_{VI}.	N_{VII}.	O_I.	$O_{II, III}$.	
74 W	893·0	850·6	752·1	208·1	191·3	169·8	138·3	133·7	44·1	38·0	33·0	18·8	18·4	2·9	2·8	5·7	5·2	74 W
73 Ta	862·2	820·8	728·0	199·5	183·2	162·9	132·2	127·8	41·2	35·3	30·9	17·8	16·6	2·2	1·9	4·7	4·4	73 Ta
72 Hf	832·0	791·3	704·5	191·8	175·9	156·9	126·6	122·6	40·0	34·0	29·8	16·8	16·0	1·6	1·4	4·8	4·3	72 Hf
71 Cp	802·6	762·9	681·2	183·8	168·6	150·9	120·9	117·2	36·9	32·5	28·7	16·1	14·7	1·0	0·7	4·2	4·0	71 Cp
70 Yb	774·6	735·4	659·2	177·1	162·2	145·8	116·4	112·8	36·2	31·0	27·5	14·9	14·2	0·9	0·6	—	3·6	70 Yb
69 Tm......	746·8	708·8	637·3	170·3	155·5	140·2	111·7	108·4	34·4	30·0	26·6	14·5	13·2	0·9	0·4	—	3·8	69 Tm
68 Er	719·6	682·6	615·9	163·6	148·8	134·7	107·2	104·0	33·1	28·4	24·9	13·7	12·6	0·9	0·3	3·9	3·9	68 Er
67 Ho	693·2	657·1	594·7	157·1	142·7	129·3	102·7	99·8	31·8	26·9	23·8	12·8	12·0	0·8	0·2	—	2·7	67 Ho
66 Dy	667·7	632·2	574·2	151·2	136·9	124·5	98·5	95·8	31·0	26·1	23·2	12·2	11·6	0·8	—	3·1	3·2	66 Dy
65 Tb	642·6	608·3	553·9	145·0	131·0	119·6	94·2	91·6	29·4	24·3	22·0	11·4	11·1	—	—	3·5	2·6	65 Tb
64 Gd	618·2	584·6	533·9	139·0	125·5	115·0	90·0	87·7	28·6	23·0	21·0	11·0	10·8	—	—	4·0	3·3	64 Gd
63 Eu	594·3	561·5	514·4	133·1	120·2	110·3	86·0	83·8	27·2	22·6	20·4	10·7	10·4	—	—	3·6	2·9	63 Eu
62 Sm	571·2	538·9	495·0	127·2	114·7	105·8	81·9	79·9	25·9	20·9	19·5	10·0	9·8	—	—	3·1	2·8	62 Sm
60 Nd	526·2	495·5	457·8	116·5	104·8	96·8	74·2	72·5	23·7	19·2	17·8	9·2	9·2	—	—	3·1	2·7	60 Nd
59 Pr	504·3	474·6	439·6	111·6	99·3	92·4	70·3	68·9	22·7	18·3	16·9	8·9	8·7	—	—	3·1	2·3	59 Pr
58 Ce	483·3	454·1	421·9	106·2	94·6	88·1	66·7	65·4	21·7	17·4	16·2	8·4	8·5	—	—	3·2	2·5	58 Ce
57 La	462·9	434·2	404·4	100·7	90·0	84·0	62·9	61·7	20·5	16·5	15·4	7·8	7·8	—	—	3·0	2·3	57 La
56 Ba	441·9	414·3	386·7	95·4	84·6	79·0	58·8	57·6	18·8	14·9	14·0	6·9	6·9	—	—	3·1	2·0	56 Ba
55 Cs	421·8	394·9	369·3	89·8	79·3	74·4	54·6	53·6	17·1	13·6	12·6	5·9	5·7	—	—	1·9	1·7	55 Cs
53 I	382·6	357·6	336·0	79·2	69·1	64·8	46·8	45·9	14·0	9·4		4·1	4·1	—	—	—	0·7	53 I
52 Te	364·1	340·3	320·1	74·5	64·4	60·5	43·3	42·4	12·7	8·9		3·6	3·2	—	—	—	0·5	52 Te
51 Sb	346·1	323·6	305·3	70·4	60·0	56·4	40·4	39·7	12·1	7·2		3·3	3·2	—	—	0·8	0·1	51 Sb
50 Sn	329·4	306·3	289·5	65·3	56·2	53·1	36·5	35·9	10·2	7·1		2·0	1·9	—	—	0·2	0·6	50 Sn

Table VIII.

The Square Root of the Values of Energy Levels ($\sqrt{T/R}$).

	L_I.	L_{II}.	L_{III}.	M_I.	M_{II}.	M_{III}.	M_{IV}.	M_V.	N_I.	N_{II}.	N_{III}.	N_{IV}.	N_V.	N_{VI}.	N_{VII}.	O_I.	$O_{II, III}$.	
74 W ……	29·883	29·166	27·425	14·43	13·83	13·03	11·76	11·56	6·64	6·17	5·75	4·34	4·28	1·71	1·67	2·38	2·29	74 W
73 Ta ……	29·362	28·650	26·982	14·13	13·54	12·76	11·50	11·31	6·42	5·94	5·56	4·21	4·08	1·50	1·39	2·18	2·10	73 Ta
72 Hf ……	28·844	28·130	26·541	13·85	13·26	12·53	11·25	11·07	6·32	5·83	5·46	4·09	4·00	1·24	1·19	2·19	2·08	72 Hf
71 Cp ……	28·331	27·620	26·101	13·56	12·98	12·28	11·00	10·82	6·08	5·70	5·36	4·01	3·84	1·0	0·8	2·04	2·01	71 Cp
70 Yb ……	27·831	27·118	25·675	13·31	12·74	12·08	10·79	10·62	6·02	5·57	5·24	3·86	3·77	1·0	0·8	—	1·90	70 Yb
69 Tm ……	27·327	26·622	25·245	13·05	12·47	11·84	10·57	10·41	5·87	5·47	5·16	3·81	3·64	1·0	0·7	—	1·94	69 Tm
68 Er ……	26·826	26·127	24·816	12·79	12·20	11·61	10·35	10·20	5·75	5·33	4·99	3·70	3·55	0·9	0·6	1·98	1·97	68 Er
67 Ho ……	26·328	25·634	24·387	12·53	11·94	11·37	10·14	9·99	5·64	5·19	4·88	3·57	3·46	0·9	0·4	—	1·63	67 Ho
66 Dy ……	25·840	25·144	23·963	12·29	11·70	11·16	9·93	9·79	5·57	5·11	4·81	3·49	3·41	0·9	—	1·77	1·79	66 Dy
65 Tb ……	25·349	24·664	23·534	12·04	11·45	10·94	9·70	9·57	5·42	4·93	4·69	3·37	3·33	—	—	1·87	1·61	65 Tb
64 Gd ……	24·864	24·179	23·107	11·79	11·20	10·73	9·49	9·36	5·34	4·80	4·59	3·32	3·29	—	—	2·00	1·81	64 Gd
63 Eu ……	24·379	23·697	22·679	11·54	10·97	10·50	9·27	9·15	5·21	4·76	4·51	3·27	3·22	—	—	1·88	1·69	63 Eu
62 Sm ……	23·899	23·214	22·249	11·28	10·71	10·28	9·05	8·94	5·08	4·57	4·41	3·16	3·14	—	—	1·75	1·68	62 Sm
60 Nd ……	22·959	22·260	21·395	10·79	10·24	9·84	8·61	8·52	4·87	4·39	4·22	3·03	3·03	—	—	1·76	1·66	60 Nd
59 Pr ……	22·456	21·785	20·967	10·57	9·96	9·61	8·39	8·30	4·77	4·27	4·12	2·98	2·96	—	—	1·75	1·51	59 Pr
58 Ce ……	21·984	21·310	20·541	10·30	9·72	9·39	8·17	8·09	4·66	4·17	4·02	2·89	2·92	—	—	1·79	1·57	58 Ce
57 La ……	21·514	20·837	20·108	10·03	9·49	9·17	7·93	7·86	4·53	4·06	3·92	2·79	2·79	—	—	1·72	1·52	57 La
56 Ba ……	21·022	20·355	19·664	9·77	9·20	8·89	7·67	7·59	4·34	3·86	3·74	2·63	2·62	—	—	1·75	1·43	56 Ba
55 Cs ……	20·537	19·872	19·218	9·47	8·90	8·62	7·39	7·32	4·14	3·68	3·55	2·43	2·40	—	—	1·4	1·3	55 Cs
53 I ………	19·560	18·910	18·329	8·90	8·31	8·05	6·84	6·78	3·74	3·07		2·01	2·02	—	—	—	0·8	53 I
52 Te ……	19·082	18·446	17·891	8·63	8·02	7·78	6·58	6·51	3·56	2·98		1·89	1·80	—	—	—	0·7	52 Te
51 Sb ……	18·605	17·988	17·472	8·39	7·74	7·51	6·36	6·30	3·47	2·69		1·81	1·78	—	—	0·9	0·4	51 Sb
50 Sn ……	18·149	17·500	17·016	8·08	7·50	7·29	6·04	5·99	3·19	2·66		1·41	1·37	—	—	0·5	0·7	50 Sn

By means of these data, the values of the spectral terms T divided by Rydberg's constant R and those of the square root of the same for different energy levels of each element were calculated, and are given in Tables VII. and VIII.* respectively. The levels M_I, M_{IV}, N_I, and N_{VI} may be computed in different ways, but those processes which involve the use of frequencies of the weaker and more diffuse emission lines as well as absorption edges were avoided, and the following formulæ were used :—

$$M_I = L_{III} - L_l, \quad M_{IV} = L_{III} - L_{\alpha_2},$$
$$N_I = L_{III} - L_{\beta_6}, \quad N_{VI} = L_{III} - L_{\alpha_2} - M_\beta.$$

Just as in the paper by Bohr and Coster we plot the value $\sqrt{T/R}$ as a function of the atomic number Z, as shown in fig. 3, where, however, the L-curves have been omitted, owing to the very large values of their energy levels. In the figure the black dots represent the levels with odd suffixes and the white circles those with even suffixes. In the case of the L- and M-levels the points lie on smooth curves, which have distinct and sudden bends at La (57) and Cp (71), a feature which was emphasized by Bohr and Coster and which will be discussed later. On the other hand, the points corresponding to the N- and O-levels have small irregularities. This is perhaps due to the fact that the term values here, which are obtained by the difference between absorption and emission frequencies, are small, and consequently the errors of both these measurements are revealed more prominently than in the case of the L- and M-levels.

In this connexion the following remarks as regards the accuracy of term values may be made. First of all we have the error in the measurements of the L-absorption spectra. This has been already pointed out and is rather large for L_I. The values of the other levels are calculated from the frequencies of the L-absorption edges by means of L- or M-emission lines, some of which are weak and diffuse, for instance, L_l, L_{β_6}, and L_{β_7} †. Thus the errors in the values of some levels are fairly high, and we may consider them generally twice as large as those in the L-absorption edges. Especially as regards the L_{β_7} line, which is used for the calculation of the O_I-level, there are some uncertainties in its identification in the case of certain elements[*], because this weak line lies quite close to another weak line and even crosses it, if we follow from one element to another. This may perhaps account for the irregularity of the values of the O_I-levels. But, of course, we cannot draw any definite conclusion as to the certainty of the explanation of this and other irregularities without a further accurate test, and especially without a closer systematic investigation of the emission lines. The writer is at present occupied with such an investigation.

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* Some values which were improved by the further measurements of the present writer are given differently in these tables from those in our previous work. The difference is, however, in most cases within the limit of the experimental error.

† As regards the accuracy of emission lines, see Coster, Phil. Mag. xliii. p. 1084 (1922).

At the end of this paragraph another remark may be added that the frequency of absorption edges, as is well known now, is influenced by the chemical and physical state under which the element in question exists. The maximum difference is about 1·0 unit in frequency between different compounds for the K-absorption of P, S, Cl[†], Ti, Va, Cr, and Mn, and the L-absorption of Sn, Sb, Te, and I[‡]. As mentioned above, the present experimental results were obtained with different sorts of compounds for the different elements. The tables given above consequently contain uncertainties as to their absolute values to the extent that they give the values obtained not with pure elements, but with compounds. But from the results we may conclude that the general features of the curves, which are of primary importance and will be discussed in the next paragraph in connexion with the natural system of the elements, is not thereby materially affected.

Discussion of the Results.

Following the classification adopted by Bohr and Coster, each level in fig. 3 is characterized by a symbol $n(k_1, k_2)$, where k_2 is either equal to k_1 or equal to k_1-1. The appearance of any such level is assumed to be conditioned by the presence in the normal atom of electronic orbits for which the principal quantum number is equal to n, and for which the azimuthal quantum numbers are equal to k_1 and k_2. Any pair of levels for which the values of n and k_1 are the same, whereas the values of k_2 differ by one unit, form a so-called relativity doublet. For such doublets the distance between the corresponding curves increases in general rapidly with the atomic number. Pairs of levels for which n and k_2 are equal, but for which k_1 differs by one unit, form the so-called screening doublets, which show themselves by the remarkably parallel course of their curves. The theoretical explanation of these features of the curves presents at present unsolved problems, for the discussion of which the reader is referred to the paper by Bohr and Coster. Here we shall confine ourselves to a discussion of those properties of the curves which may be brought in direct connexion with the gradual development of the electronic groups due to the appearance of orbits of new types with increasing atomic number. The addition of such new orbits can be traced partly by the appearance of new

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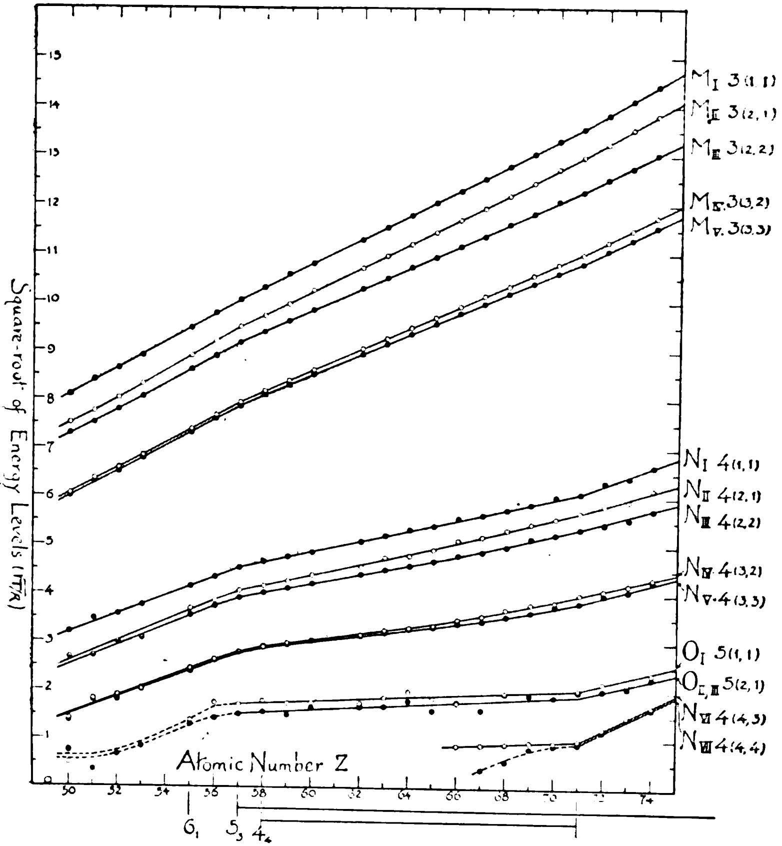
[*] This was kindly pointed out by Dr. D. Coster during the preparation of this paper. Compare Coster, Phil. Mag. xliv. p. 554 (1922).

[†] Lindh, Dissertation Lund (1923).

[‡] Coster, *Zs. für Phys.* xxv. p. 83 (1924). Tandberg, *Arkiv för Matematik, Astronomi och Fysik*, xviii. no. 14, p. 1 (1924).

Fig. 3.



X-ray levels, and partly by changes in the rate of variation with the atomic number of levels already present. Within the region of elements investigated in this paper we shall, according to Bohr's theory, expect the first appearance of 6_1 orbits at Cs (55), of 5_3 orbits at La (57), and of 4_4 orbits at Ce (58). Now, the orbits of the 6_1 type correspond within the whole sequence of elements under consideration only to valence electrons moving for the most part in the exterior region of the atom, and it is therefore easily understood that it has not been possible with certainty to detect the appearance of the corresponding new levels or to recognize any marked influence on the other levels due to the addition of such orbits. With the 4_4 orbits the situation is quite different. Their appearance in the atom marks the final states of completion of the 4-quantum group, and according to the theory gives rise to the presence of the family of rare earths within the periodic table. As mentioned, Bohr and Coster drew attention to a number of anomalies in the course of the level curves in the region of this family of elements which could all be accounted for on the basis of the theoretical expectation that the added 4-quantum orbits will find their position in a region of the atom closer to the nucleus than that region where the electrons in 5- and 6-quantum orbits are moving during the greater part of their revolutions. The present measurements allow us to examine these anomalies with greater accuracy, and to obtain a general support of the conclusions of Bohr and Coster.

In conformity with the classification of fig. 3, the levels which are directly conditioned by the presence of electrons in 4_4 orbits are N_{VI} and N_{VII}. According to the theory, the stage in the development in the 4-quantum group, to which the binding of electrons in such orbits gives rise, is initiated in Ce (58) and is completed in Cp (71), which forms the last of the rare earth elements. This development takes place, so to speak, in competition with the binding of the valence electrons; and we must therefore expect that as long as it goes on, the work necessary to remove a 4_4 electron from the atom will remain quite small, about the same order as that for valence electrons 6_1 and smaller than that for 5_1 and 5_2 electrons, throughout the whole rare earth family, and first start to increase steadily at the element Hf (72). This is brought out clearly in the course of the N_{VI} and N_{VII} curves, which show a sharp upwards bend at Cp (71). As we know from older measurements, these curves will cross the O-curves somewhere between Ir (77) and Tl (81). As indicated in the figure, the curve N_{VII} below Cp (71) seems to diverge from the N_{VI} curve. This is quite unusual because these two curves form what is called a relativity doublet; the divergence, however, seems to be too large to be explained by systematic experimental errors. Whether this anomaly has real existence, and points to special features connected with the development of the 4-quantum group, remains, however, to be settled.

As regards the other levels, the influence of the development of the 4-quantum group is perhaps most strikingly shown in the O-levels. The irregularities in the points representing the measurements are in this case probably due to accidental errors, but the figure nevertheless brings out clearly that these levels during the whole region of the rare earth family remain very nearly constant. This is explained, according to the theory, by the circumstance that the added 4_4 electrons will move in a region of the atom lying within the region in which the 5_1 and 5_2 electrons move during the greater part of their revolutions. The effect of the increasing nuclear charge on the strength of binding of these electrons will therefore in the interval between La (57) and Cp (71) be nearly balanced by the screening of the added electrons in the 4-quantum orbits. The O_I- and $O_{II,\,III}$-curves have, furthermore, a distinct bending at Ba (56) instead of La (57), at which all other curves have a marked bend, although there seems to be a very slight indication of bending at Ba (56) for some levels. This unique feature of the O-levels is perhaps caused by the first binding of the 5_3-electron at La (57), the effect of which will not be so much felt by other levels as by the 5-quantum orbits.

Apart from small anomalies probably due to accidental errors, the levels N_I, N_{II}, N_{III}, N_{IV}, and N_V, which are conditioned by the presence of 4_1, 4_2, and 4_3 orbits, show a smooth course with a distinct bend at La (57) and a less pronounced bending at Cp (71). On the theory this is accounted for by the diminishing influence on the strength of binding of these electrons, due to the repulsive forces from the 4_4 electrons, which move in the same region in the atom as the 4_1, 4_2, and 4_3 electrons, and which are just added in the interval between La (57) and Cp (71). Attention may be called to various systematic deviations in the relationship between neighbouring N-curves from what is usually expected from the behaviour of relativity and screening doublets. For instance, the curves N_{IV} and N_V seem to draw closer after Hf (72), and there is an indication that the N- and O-curves show certain irregularities below

X (54), which are perhaps to be connected with the development of the 5-quantum groups which are brought to partial completion at X (54). Whether these facts represent the real nature of things or come merely from the experimental errors, it is difficult to decide at present.

The development of the 4-quantum group can, moreover, be clearly traced in the M-levels, since all the curves representing these levels show bends at La (57) and Cp (71). The M-levels are conditioned by electrons in 3-quantum orbits moving still closer to the nucleus than the 4-quantum electrons. In the effect under consideration we have to do with what is denoted by Bohr and Coster as the outer screening effect, which arises from the balancing influence on the work necessary to remove a 3-quantum electron, due to the increase in the strength of the binding of the electrons in the 4-quantum orbits resulting from this removal.

In conclusion, the author wishes to thank Professor N. Bohr for his constant encouragement during the experiment, and for his invaluable discussion and criticism during the preparation of this paper. His thanks are also due to Dr. D. Coster for his unfailing kindness in giving instructive advice throughout the work.

Universitetets Institut for teoretisk Fysik,
Copenhagen, November 1924.

LIX. *The Motion of Free Electrons in Black Body Radiation, and the Interaction between Radiation and Matter.* By G. Breit *.

Introduction.

THE motion of free electrons in black body radiation has been discussed by Fokker †, who showed that if the waves constituting black body radiation have random phases, the mean kinetic energy of the electron's motion is not $3/2kT$ but about $1/24$ of this value. The problem has been considered again by Pauli ‡, who discusses the motion of electrons on the supposition that quanta are absorbed bodily by electrons and that simultaneously with the $\left(\begin{matrix}\text{absorption}\\ \text{emission}\end{matrix}\right)$ of a quantum $h\nu$ a momentum $h\nu/c$ is $\left(\begin{matrix}\text{absorbed}\\ \text{emitted}\end{matrix}\right)$ by the electron. Pauli obtains $3/2kT$ for the

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[*] Communicated by the Author.

[†] Dissertation Leiden, 1913; *Arch. Néerl.* (3 *a*) iv. p. 379 (1918).

[‡] *Zeits. f. Phys.* xviii. p. 273.

mean kinetic energy. It is generally supposed that $3/2kT$ is the proper value for the mean kinetic energy of free electrons in black body radiation, and the present situation is therefore such as to condemn the classical wave theory in favour of the light-dart theory from considerations based on the motion of free electrons alone.

This evidence in favour of light darts is re-examined below. In § 1 the problem of the statistical equilibrium of free electrons is considered as a special case of a coupled quantized system, and the *a priori* necessity of having the mean kinetic energy equal to exactly $\frac{3kT}{2}$ is questioned.

In § 2 it is shown that Fokker's treatment is concerned only with one type of motion, which may be termed the slow surging or progressive type. In addition to this, there is a rapidly vibratory type. A numerical estimate of its value shows it to be small at ordinary temperatures. It is pointed out that Fokker's result must be modified if there are systematic phase relations between the waves constituting the radiation. Reasons are given for looking at the term ρ^2/ν^2 in the numerator of Fokker's result as a special case of $\alpha\bar{\epsilon^2}/h$, where $\bar{\epsilon^2}$ is Einstein's expression for the average square of the fluctuation of energy density applied to unit volume, which for Planck's formula has the expression $h\nu\rho + h\rho^2/\alpha\nu^2$ and for the Rayleigh-Jeans relation degenerates into $h\rho^2/\alpha\nu^2$. It is shown that with this change Fokker's formula gives exactly $3/2kT$ for the mean kinetic energy of free electrons.

In § 3 the meaning of the modification introduced in § 2 is examined, and statistical relations are derived which must be satisfied in order to make the modification valid.

In § 4 the problem is discussed from the point of view of very loosely bound electrons, and it is shown that the case is not essentially distinct from the case of Bohr atoms such as are discussed by Einstein*, and the writer's remarks† applied to Bohr's atoms are translated into corresponding statements for free electrons. It is shown that for both problems the essential condition is that the relation between the electric force on the electron (which does the work) and the motional force due to the magnetic intensity (which gives the radiation pressure) should be the same as on the classical theory. This suggests thinking of the transmission of energy and momentum in terms of old-fashioned waves, and regarding the absorbed energy as *force* × *distance* where the force is the force due to the wave and the distance is closely allied to the actual distance traversed by the electron. Similarly, the momentum imparted by the wave is calculable from the motional intensity $\frac{e}{c}[\mathbf{v}, \mathbf{h}]$, where $\mathbf{v}$ is taken for the same motion which is considered in the calculation of the absorbed energy. This motion is shown presently to be not exactly the electronic motion, but to be more closely allied with Bohr's corresponding motion.

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* Einstein, *Phys. Zeitschr.* xviii. p. 121 (1917).

† G. Breit, Phys. Rev. pp. 313–319 (1923).

In § 5 the difficulty of applying the wave theory to the photoelectric effect is discussed, and it is shown that the difficulty disappears if the absorption is conceived of on the lines of § 4. The present point of view differs from the older in looking at the absorbed energy as *force × distance* instead of considering the flux of Poynting's vector across a section of the wave of atomic dimensions. The Principle of Conservation of energy is shown to be satisfied by the postulated mechanism. It is shown that the view proposed may be looked at as a generalization of Bohr's Principle of Correspondence, provided the action of the radiation force $\frac{2}{3}\frac{e^2}{c^3}\ddot{v}$ on the atom is *unclassical* to the same extent as the action of the external wave. The *unclassical* nature of both consists in a cumulative action on the atom for a time long in comparison with the period of the wave without affecting the motion of the *equivalent corresponding* mechanism, which is an harmonic oscillator of a frequency equal to the emission frequency and of an amplitude equal to a mean amplitude of the motion of the electron between the two states. The integral actions, however, are the same as on the classical theory. This is in agreement with phenomena of dispersion. The view proposed also explains the very high absorption of γ rays by the atom in which the γ rays have been produced, which is found from a study of γ-ray spectra by Ellis and Meitner.

§ 1. The problem of free electrons subjected to the action of black body radiation is a special case of the general problem of investigating the result of the action of a system (A) on a system (B). [The system (A) is the radiation. The system (B) is the electron.] The essential characteristic of our case is that the number of degrees of freedom in (A) is large and that in (B) is small. The approximation which is made by Fokker in the problem of free electrons, and which has always been made by everyone in the problem of resonators and atoms, is that one can regard the motion of (A) as unaffected by (B), and from the statistically known state of (A) calculate the so far statistically unknown state of (B). If on using the Planck radiation formula the classical interactions do not give the correct mean kinetic energy for free electrons (B), then one must conclude that the interactions between (A) and (B) are not classical. This is the claim made for the special case of free electrons from Fokker's calculation by Pauli.

The cornerstone of this line of reasoning is the necessity of having the mean kinetic energy of (B) equal to $3/2\,k\mathrm{T}$, which is the value it would have if it were not coupled to (A). The necessity for this is not at all obvious. As soon as an interaction between (A) and (B) is introduced, we cease to have two separate systems, and we must deal with a coupled system. In this any of the old coordinates of (A) implies something as to the state of (B), and *vice versa* *.

From a purely formal point of view we must quantize the coupled system and apply quantum statistics to the result. If the motion of the coupled system (AB) is multiply periodic, this can always be done. In the very process of quantization the interactions between (A) and (B) are of necessity taken as classical. From this point of view it seems more proper to question the validity of the statement that the mean kinetic energy of a "free" electron is $3/2\,k\mathrm{T}$ rather than the classical nature of the interactions, because the unclassical element comes in through the quantization of the coupled system (AB) and not through the unclassical nature of the interactions. The view maintained here is that an electron put in black body radiation cannot be properly called *free* because it is coupled to the radiation.

The fact that the radiation force $\frac{2}{3}\frac{e^2}{c^3}\ddot{v}$ is known to be inapplicable to the Bohr atom is, of course, an objection to the formal viewpoint just sketched. So far as the problem of free electrons is concerned, we can imagine a fictitious system in which a dissipative force $\frac{2}{3}\frac{e^2}{c^3}\ddot{v}$ is operative for the electron and in which an equal and opposite reaction is exerted on the rest of the system in such a way as to keep the resultant system conservative.

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* Jeans, in his papers: Phil. Mag. xviii. p. 209 (1909), xvii. p. 773 (1909), xxvii. p. 14 (1914), deals with the interaction of free electrons with radiation. However, he does not discuss the radiation pressure effects.

Even though we cannot accept without further proof the necessity for having $\frac{1}{2}mv^2 = \frac{3}{2}kT$ for electrons in black body radiation, we have some reason for expecting that electrons emerging by chance from a space occupied by black body radiation into free space should satisfy this condition. It may be shown that it is probable that Fokker's calculation deals with that part of the motion which survives after the escape of the electron.

The approximate assumption which is very conveniently made by Fokker is that the motion of (A) is not modified appreciably by the presence of (B). This amounts to saying that the coupling between (A) and (B) is loose. The problem of loosely-coupled systems has been considered by Burgers*, who showed that the quantizations become independent, and that the perturbations are in the limit calculable on a purely classical basis. From this point of view it is again questionable that the apparent violation of statistical mechanics is to be attributed to the classical interactions.

§ 2. The motion of an electron in the radiation field is thought of most simply by depriving it of some of its degrees of freedom. To start with, let us constrain the electron to move in a straight line. The calculation of $\frac{1}{2}m\overline{v^2}$ is very clear in this case. We consider a very long period of time T, and resolve the component of the electric intensity along the line of motion into a Fourier series with T as period. If T is very great, the effects of the initial motion are of no importance and the electron may be thought of as executing forced vibrations under the action of each of the terms in the expansion of the electric intensity. Using the Heaviside-Lorentz notation, the equation of motion is

$$m\ddot{x} - \frac{e^2}{6\pi c^3}\dddot{x} = ed_x, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

from which it can be shown that the mean kinetic energy is for Planck's radiation formula

$$\frac{\overline{m\dot{x}^2}}{2} = \frac{1}{\pi}\int_0^\infty \frac{mh\nu d\left(e^2\nu/(3c^3)\right)}{\left(e^{\frac{h\nu}{kT}}-1\right)\left(m^2+\left(\frac{e^2\nu}{3c^3}\right)^2\right)}. \quad . \quad . \quad (2)$$

If in this formula $h \rightarrow 0$, $\frac{\overline{m\dot{x}^2}}{2} \rightarrow \frac{kT}{2}$. This means that for the Rayleigh-Jeans radiation $\frac{kT}{2}$ is obtained. However, for ordinary temperatures the value of the expression on the right is only a very small fraction of $\frac{kT}{2}$, for its order of magnitude is that of $kT\tan^{-1}\left(\frac{e^2\nu}{3mc^3}\right)$, where $\nu \simeq \frac{kT}{h}$. If $\nu=10^{15}$, the energy of the motion is only about $10^{-7}kT$.

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* Burgers, Dissertation Leiden, p. 216; *Versl. Akad. Amst.* xxvi. p. 702 (1917).

If the energy of the electron having one degree of freedom had to be $\frac{kT}{2}$, the calculation of Fokker would be unnecessary, for the above simple formula gives less than the required value. An inspection of the above formula shows, however, the presence of the factor $x/(e^x-1)$, $(x=h\nu/kT)$, so familiar in the quantum theory of specific heats. The reason why the kinetic energy is too small is that the electron is to be considered as coupled to the radiation, and that its motion is to be thought of as resolved into harmonic vibrations each of which is associated with a general mode of vibration of the coupled system as a whole (§ 1). The small value of the vibratory energy of the electron is in this case a natural consequence of the small value of the vibratory energy of the higher frequencies in the black body spectrum. The small value is not in contradiction with the statistical requirement that free electrons having Maxwell's distribution—then subjected to the action of black body radiation, and then removed from the radiation—should remain with Maxwell's distribution. For there are no radiation pressure-effects on the constrained electron, and the vibratory motion is so small that the electron has a negligible chance of leaving the radiation field.

The type of motion illustrated by the constrained electron is thus seen to be powerless for giving a criterion in favour of or against light-darts. It is not the type considered by Fokker.

We suppose next that the line of constraint OX is allowed to move perpendicularly to itself in the plane OXY. We imagine the line endowed with a mass $-m+M \gg m$. The equations of motion are :—

$$\left.\begin{aligned} m\ddot{x}-\frac{e^2\dddot{x}}{6\pi c^3} &= e(d_x+\dot{y}h_z/c), \\ M\ddot{y}-\frac{e^2\dddot{y}}{6\pi c^3} &= e(d_y-\dot{x}h_z/c). \end{aligned}\right\} \quad . \quad . \quad . \quad (3)$$

If M is very great, the values of $\dot{y}$ are very small. As a first approximation, we may consider the vibratory motion of x to depend on d_x. To this approximate value of x there corresponds a value of $\dot{x}$ which, when substituted into the second of the two equations (3), gives rise to surging motions of y (due essentially to combination-frequency terms arising from $-\dot{x}h_z/c$). These are the terms taken into account by Fokker. Making the calculation for three degrees of freedom, and assuming that this involves the addition of the effects due to each, he gets a result equivalent to

$$\tfrac{1}{2}m\overline{v^2} = \frac{3c^3}{64\pi} \cdot \frac{\int_0^\infty \frac{\rho^2}{\nu^2} d\nu}{\int_0^\infty \rho \, d\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\rho(\nu)d\nu$ is the energy density in the frequency range $d\nu$, which on substituting Planck's expression for ρ becomes

$$\tfrac{1}{2}m\overline{v^2} = \tfrac{3}{8}k\mathrm{T} \frac{\int_0^\infty \frac{x^4}{(e^x-1)^2} dx}{\int_0^\infty \frac{x^3}{e^x-1} dx} = \tfrac{3}{2}k\mathrm{T} \times 0{\cdot}0417. \quad . \quad (4')^{*}$$

Formula (4) Fokker derives from his equation

$$\tfrac{1}{2}m\overline{v^2} = \frac{\overline{\mathrm{X}^2} + \overline{\mathrm{Y}^2} + \overline{\mathrm{Z}^2}}{4\mathrm{Q}\tau},$$

in which (X, Y, Z) is the momentum imparted to the electron by the electromagnetic radiation in time τ, and $\mathrm{Q}v$ is the systematic resisting force exerted by the radiation on an electron moving with velocity v. The numerator in (4) is thus essentially

$$\frac{\overline{\mathrm{X}^2}}{\tau} = \frac{2}{9}\left(\frac{e^2}{4\pi mc}\right)^2 \int_0^\infty \frac{\rho^2}{\nu^2} d\nu,$$

while the denominator is

$$4\mathrm{Q} = \frac{4e^4}{6\pi c^5 m^2} \int_0^\infty \left(-\frac{\nu}{3}\frac{\partial\rho}{\partial\nu} + \rho\right) d\nu = \frac{2}{9}\,\frac{4e^4}{\pi c^5 m^2} \int_0^\infty \rho \, d\nu \;\dagger.$$

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* h is seen to be absent in this formula. This in itself raises a suspicion as to its validity.

† This transformation is valid only if $\nu\rho$ vanishes both at $\nu = \infty$ and at $\nu = 0$. Thus the transformation is not applicable in the case of the formula of Rayleigh-Jeans.

The term 4Q is obtained by considering the reaction on the electron due to the radiation in a very long time during which the electron moves with finite average velocity. The problem is essentially that of forced vibrations and of transforming the radiation field to a moving system of reference. There is thus little reason for doubting the expression for 4Q.

The origin of X^2/τ is, in cross-product terms,

$$\frac{1}{\tau}\left(\frac{e^2}{2\pi m\nu}\sum_{1,2}\int_t^{t+\tau}[\mathbf{d}_1,\mathbf{h}_2]_y\,dt\right)^{2}\,{}^{*},$$

where $(\mathbf{d}_1,\mathbf{h}_1)$, $(\mathbf{d}_2,\mathbf{h}_2)$ are the electric and magnetic intensities in two waves of neighbouring frequencies, and [ ] denotes the vector product. If there are no phase relations between the various waves, the product terms between the various terms in the summation for $\overline{X^2}/\tau$ need not be taken into account. They are actually neglected by Fokker.

Now, it is known that Einstein's fluctuation formula

$$\overline{\epsilon^2} = h\nu\rho + h\rho^2/(\alpha\nu^2)$$

is inconsistent with a picture of black body radiation based on waves with random phase differences †. We must admit, therefore, the possibility of some phase relations in a manner similar to Planck's ‡.

Since the numerator of (4) contains ρ^2/ν^2 just as the classical part of ϵ^2, and since the origin of $\overline{X^2}/\tau$ is closely similar to the origin of ϵ^2 (one arising from Poynting's vector and the other from the energy density), we may provisionally expect that the contribution to $\overline{X^2}/\tau$ due to the frequency range $d\nu$ is changed by taking into account the phases in the same proportion as $\overline{\epsilon^2}$ is changed. This ratio is

$$1+\alpha\nu^3/\rho = \epsilon^x, \quad (x = h\nu/kT).$$

Hence, from (4′),

$$\tfrac{1}{2}\overline{mv^2} = \tfrac{3}{8}kT\,\frac{\displaystyle\int_0^\infty \frac{x^4e^x}{(e^x-1)^2}\,dx}{\displaystyle\int_0^\infty \frac{x^3}{e^x-1}\,dx}\,§ = \tfrac{3}{2}kT. \quad . \quad . \quad . \qquad (5)$$

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* See equation (7) below.

† H. A. Lorentz, 'Les Théories Statistiques en Thermodynamique.' (Teubner, 1916.)

‡ M. Planck, *Ann. der Phys.* lxxiii. p. 272 (1924).

§ $$4\int_0^\infty \frac{x^3}{e^x-1}\,dx = -\int_0^\infty x^4\frac{d}{dx}\left(\frac{1}{e^x-1}\right)dx = \int_0^\infty \frac{x^4e^x}{(e^x-1)^2}\,dx.$$

To summarize this paragraph, the numerator of Fokker's formula (4) must be modified if the waves of the radiation are to conform with the thermodynamically derivable expression $\overline{\epsilon^2}$ of Einstein. Regarding the changes in ϵ^2 and in $\overline{X^2}/\tau$ as proportional to each other, Fokker's result becomes equal to $3/2kT$.

§ 3. We must now inquire into the meaning of the hypothesized equivalence of the effects of phase relations on $\overline{X^2}/\tau$ and on ϵ^2.

Let us calculate $\overline{\epsilon^2}$. We consider the radiation field inside a sphere. The energy density is given by $\frac{1}{2}(d^2+h^2)$. The value of **d** at any point is the sum of the values due to the various component waves. The value of ϵ which we must consider is therefore

$$\epsilon = \Sigma\,(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)\iiint_S \cos 2\pi\left(\nu_1 t - \frac{l_1x+m_1y+n_1z}{\lambda_1} - \psi_1\right)$$
$$\times \cos 2\pi\left(\nu_2 t - \frac{l_2x+m_2y+n_2z}{\lambda_2} - \psi_2\right) dx\,dy\,dz,$$

where **d**, **h** are vector amplitudes; ν, λ, (l, m, n), ψ are the frequency, wave-length, direction cosines, and phase of each wave; and where the integration is extended over the interior of the sphere. The summation is extended over all combinations (1, 2), each *combination* being taken once. We have, on performing the integration,

$$\frac{1}{3}\frac{\epsilon}{4\pi r^3/3} = \Sigma\,\tfrac{1}{2}(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)\left(\frac{\sin x_{12}}{x_{12}^3} - \frac{\cos x_{12}}{x_{12}^2}\right)$$
$$\times \cos 2\pi((\nu_1-\nu_2)t - \psi_1 + \psi_2)$$
$$+ \Sigma\,\tfrac{1}{2}(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)\left(\frac{\sin x'_{12}}{x'^3_{12}} - \frac{\cos x'_{12}}{x'^2_{12}}\right)$$
$$\times \cos 2\pi((\nu_1+\nu_2)t - \psi_1 - \psi_2)\ ^*,$$

where

$$x_{12} = 2\pi r\sqrt{\left(\frac{l_1}{\lambda_1}-\frac{l_2}{\lambda_2}\right)^2+\left(\frac{m_1}{\lambda_1}-\frac{m_2}{\lambda_2}\right)^2+\left(\frac{n_1}{\lambda_1}-\frac{n_2}{\lambda_2}\right)^2},$$

$$x'_{12} = 2\pi r\sqrt{\left(\frac{l_1}{\lambda_1}+\frac{l_2}{\lambda_2}\right)^2+\left(\frac{m_1}{\lambda_1}+\frac{m_2}{\lambda_2}\right)^2+\left(\frac{n_1}{\lambda_1}+\frac{n_2}{\lambda_2}\right)^2}.$$

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[*] We disregard $\Sigma\frac{d^2+h^2}{4}\left(\frac{\sin x}{x^3}-\frac{\cos x}{x^2}\right)\cos 4\pi(\nu t-\psi)$ because phase relations introduced by these terms do not appear likely to give systematic effects. However, there is a possibility of there being a need of taking these into account.

Squaring the above relation and averaging, we obtain

$$\frac{1}{9}\overline{\left(\frac{\epsilon}{4\pi r^3/3}\right)^2} = \tfrac{1}{8}\Sigma\,(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)\left\{\left(\frac{\sin x_{12}}{x_{12}^3}-\frac{\cos x_{12}}{x_{12}^2}\right)^2 + \left(\frac{\sin x'_{12}}{x'^3_{12}}-\frac{\cos x'_{12}}{x'^2_{12}}\right)^2\right\}$$

$$+\tfrac{1}{4}\sum_{\nu_1-\nu_2=\nu_3-\nu_4}(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)(\mathbf{d}_3\mathbf{d}_4+\mathbf{h}_3\mathbf{h}_4)\left(\frac{\sin x_{12}}{x_{12}^3}-\frac{\cos x_{12}}{x_{12}^2}\right)$$
$$\times\left(\frac{\sin x_{34}}{x_{34}^3}-\frac{\cos x_{34}}{x_{34}^2}\right)\cos 2\pi(\psi_1-\psi_2-\psi_3+\psi_4)$$

$$+\tfrac{1}{4}\sum_{\nu_1+\nu_2=\nu_3+\nu_4}(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)(\mathbf{d}_3\mathbf{d}_4+\mathbf{h}_3\mathbf{h}_4)\left(\frac{\sin x'_{12}}{x'^3_{12}}-\frac{\cos x'_{12}}{x'^2_{12}}\right)$$
$$\times\left(\frac{\sin x'_{34}}{x'^3_{34}}-\frac{\cos x'_{34}}{x'^2_{34}}\right)\cos 2\pi(\psi_1+\psi_2-\psi_3-\psi_4)$$

$$+\tfrac{1}{4}\sum_{\nu_1-\nu_2=\nu_3-\nu_4}(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)(\mathbf{d}_3\mathbf{d}_4+\mathbf{h}_3\mathbf{h}_4)\left(\frac{\sin x_{12}}{x_{12}^3}-\frac{\cos x_{12}}{x_{12}^2}\right)$$
$$\times\left(\frac{\sin x'_{34}}{x'^3_{34}}-\frac{\cos x'_{34}}{x'^2_{34}}\right)\cos 2\pi(\psi_1-\psi_2-\psi_3+\psi_4). \quad . \; . \; . \quad (6)$$

The first summation gives rise to the term $h\rho^2/(\alpha\nu^2)$ in $\overline{\epsilon^2}$. In fact, the space positions of the wave normals 1 and 2 are entirely random. Further, the average value of $\overline{(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)^2}$ for two waves, the normals of which form a fixed angle θ but which have random polarizations, is

$$\tfrac{1}{2}(1+\cos\theta)^2(\overline{d_1^2})(\overline{d_2^2}),$$

as may be shown by integration.

The first summation is then

$$\tfrac{1}{16}\Sigma\,(\overline{d^2})^2\left\{\overline{(1+\cos\theta)^2\left(\frac{\sin x_{12}}{x_{12}^3}-\frac{\cos x_{12}}{x_{12}^2}\right)^2}\right.$$
$$\left.+\overline{(1+\cos\theta)^2\left(\frac{\sin x'_{12}}{x'^3_{12}}-\frac{\cos x'_{12}}{x'^2_{12}}\right)^2}\right\}.$$

The space averages in either of the terms are taken by assigning to the interval $(\theta, \theta+d\theta)$ the probability $\frac{1}{2}\sin\theta\,d\theta$.

Setting

$$2\pi r/\lambda = \mathrm{N},$$

we have

$$x_{12}^2 = \mathrm{N}_1^2+\mathrm{N}_2^2-2\mathrm{N}_1\mathrm{N}_2\cos\theta.$$

Thus

$$\overline{(1+\cos\theta)^2\left(\frac{\sin x_{12}}{x_{12}{}^3}-\frac{\cos x_{12}}{x_{12}{}^2}\right)^2}$$

$$=\frac{1}{2}\int_{\cos\theta=-1}^{+1}\left(1+\frac{\mathrm{N}_1{}^2+\mathrm{N}_2{}^2-x_{12}{}^2}{2\mathrm{N}_1\mathrm{N}_2}\right)^2\left(\frac{\sin x_{12}}{x_{12}{}^3}-\frac{\cos x_{12}}{x_{12}{}^2}\right)^2 d(\cos\theta)$$

$$=\frac{1}{2\mathrm{N}_1\mathrm{N}_2}\int_{|\mathrm{N}_1-\mathrm{N}_2|}^{\mathrm{N}_1+\mathrm{N}_2}\left(1+\frac{\mathrm{N}_1{}^2+\mathrm{N}_2{}^2-x^2}{2\mathrm{N}_1\mathrm{N}_2}\right)^2 x\left(\frac{\sin x}{x^3}-\frac{\cos x}{x^2}\right)^2 dx.$$

Here we need to take into account only the lowest power in $1/\mathrm{N}$. With a sufficient approximation, the integral is

$$\frac{2}{\mathrm{N}^2}\int_{|\mathrm{N}_1-\mathrm{N}_2|}^{\mathrm{N}_1+\mathrm{N}_2} x\left(\frac{\sin x}{x^3}-\frac{\cos x}{x^2}\right)^2 dx,$$

which is easily shown by partial integrations to be [on neglecting $\frac{1}{|\mathrm{N}_1+\mathrm{N}_2|}$]

$$\frac{1}{2\mathrm{N}^2}\left\{\frac{\sin^2(\mathrm{N}_1-\mathrm{N}_2)}{(\mathrm{N}_1-\mathrm{N}_2)^2}+\left(\frac{\sin(\mathrm{N}_1-\mathrm{N}_2)}{(\mathrm{N}_1-\mathrm{N}_2)^2}-\frac{\cos(\mathrm{N}_1-\mathrm{N}_2)}{\mathrm{N}_1-\mathrm{N}_2}\right)^2\right\}.$$

The average of the second term is similarly found to be zero. The contribution to the first summation in (*b*) to ϵ^2 is then

$$(\overline{\epsilon^2})_1=\frac{9}{32}\left(\frac{4\pi r^3}{3}\right)^2\sum\frac{(\overline{d_1{}^2})(\overline{d_2{}^2})}{\mathrm{N}^2}\left\{\frac{\sin^2(\mathrm{N}_1-\mathrm{N}_2)}{(\mathrm{N}_1-\mathrm{N}_2)^2}\right.$$
$$\left.+\left(\frac{\sin(\mathrm{N}_1-\mathrm{N}_2)}{(\mathrm{N}_1-\mathrm{N}_2)^2}-\frac{\cos(\mathrm{N}_1-\mathrm{N}_2)}{\mathrm{N}_1-\mathrm{N}_2}\right)^2\right\}.$$

Here

$$\sum_{d\nu}\overline{d^2}=2\rho\,d\nu,$$

since the quantities **d** are vector amplitudes.

Further,

$$\int_{-\infty}^{+\infty}\left(\frac{\sin^2 x}{x^2}+\left(\frac{\sin x}{x^2}-\frac{\cos x}{x}\right)^2\right)dx=\frac{4\pi}{3}.$$

Replacing the summation by integration, and performing one of the two integrations (remembering that the result must be divided by 2 if in the first integration the limits of $\mathrm{N}_1-\mathrm{N}_2$ are taken as $-\infty$ and $+\infty$ because each combination term we agreed to count only once in the summation),

$$\overline{\epsilon^2}=\frac{4\pi r^3}{3}\int_0^{\infty}\frac{c^3}{8\pi}\frac{\rho^2}{\nu^2}d\nu. \quad . \quad . \quad . \quad . \quad (6')$$

Thus, if it were not for the last three summations in (6), we should have per unit $d\nu$,

$$\overline{\epsilon^2} = \mathrm{V}\frac{c^3}{8\pi}\frac{\rho^2}{\nu^2},$$

where V is the volume of the sphere.

It is essential for all that follows below that at least one of the last three summations in (6) should not vanish. If all vanish, (6′) replaces (6) and there is no possibility of reconciling the wave theory with thermodynamics. The existence of the sums depends on the values of expressions of the type

$$(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)(\mathbf{d}_3\mathbf{d}_4+\mathbf{h}_3\mathbf{h}_4)\cos 2\pi(\psi_1-\psi_2-\psi_3+\psi_4).$$

Such expressions have positive values if $\psi_1-\psi_2$ is likely to be equal to $\psi_3-\psi_4$ when the inclinations of $(\mathbf{d}_1, \mathbf{h}_1)$ to $(\mathbf{d}_2, \mathbf{h}_2)$ are similar to the inclinations of $(\mathbf{d}_3, \mathbf{h}_3)$ to $(\mathbf{d}_4, \mathbf{h}_4)$. This obviously implies that waves of neighbouring frequencies travel in groups. If the elementary process of emission should consist in the creation of a group of waves, all having the same or nearly the same polarization and all confined to a sharp band of frequencies, we should expect such relations to exist, provided there is similarity in the structure of the various groups. Such a similarity is a very natural one to expect. We thus expect the second and the third summation in (6) to make finite contributions. The influence of the fourth summation is likely to be negligible. From equation (6),

$$\begin{aligned}\overline{\left(\frac{\epsilon}{\mathrm{V}}\right)^2} = \frac{1}{\mathrm{V}}\int_0^\infty \frac{c^3}{8\pi}\frac{\rho^2}{\nu^2}d\nu \\ +\tfrac{9}{4}\sum_{\nu_1-\nu_2=\nu_3-\nu_4}(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)(\mathbf{d}_3\mathbf{d}_4+\mathbf{h}_3\mathbf{h}_4)\left(\frac{\sin x_{12}}{x_{12}^3}-\frac{\cos x_{12}}{x_{12}^2}\right) \\ \times\left(\frac{\sin x_{34}}{x_{34}^3}-\frac{\cos x_{34}}{x_{34}^2}\right)\cos 2\pi(\psi_1-\psi_2-\psi_3+\psi_4), \\ +\tfrac{9}{4}\sum_{\nu_1+\nu_2=\nu_3+\nu_4}(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)(\mathbf{d}_3\mathbf{d}_4+\mathbf{h}_3\mathbf{h}_4)\left(\frac{\sin x'_{12}}{x'^3_{12}}-\frac{\cos x'_{12}}{x'^2_{12}}\right) \\ \times\left(\frac{\sin x'_{34}}{x'^3_{34}}-\frac{\cos x'_{34}}{x'^2_{34}}\right)\cos 2\pi(\psi_1+\psi_2-\psi_3-\psi_4). \\ \quad . \quad . \quad . \quad (6'')\end{aligned}$$

We shall now similarly consider the effects for $\overline{\mathrm{X}^2}/\tau$. The equations of motion are

$$m\ddot{x}-\frac{e^2}{6\pi c^3}\dddot{x} = ed_x+\frac{e}{c}[\mathbf{v},\mathbf{h}]_x.$$

To a first approximation in the complex notation

$$\dot{x} = ed_x/(2\pi i \nu m), \quad \text{where} \quad i = \sqrt{-1}.$$

We must consider the value of X given by

$$\mathrm{X} = \frac{e^2}{2\pi m\nu c} \Sigma \int_t^{t+\tau} \Big\{ [\mathbf{d}_1, \mathbf{h}_2]_x \cos\left(2\pi\nu_1 t - 2\pi\psi_1 - \frac{\pi}{2}\right) \times \cos 2\pi(\nu_2 t - \psi_2) + [\mathbf{d}_2, \mathbf{h}_1]_x \cos 2\pi(\nu_1 t - \psi_1) \cos\left(2\pi\nu_2 t - 2\pi\psi_2 - \frac{\pi}{2}\right)\Big\} dt.$$

Squaring, averaging, and neglecting terms in $(\nu_1 + \nu_2)^{-1}$, as well as higher-order terms in $\nu_1 - \nu_2$, in the usual manner,

$$2\left(\frac{4\pi mc}{e^2}\right)^2 \frac{\overline{\mathrm{X}}}{\tau} = \sum \frac{([\mathbf{d}_1, \mathbf{h}_2]_x - [\mathbf{d}_2, \mathbf{h}_1]_x)^2}{\nu^2} \frac{\sin^2 2\pi(\nu_1 - \nu_2)\tau}{\tau(2\pi(\nu_1 - \nu_2))^2}$$
$$+ 2 \sum_{\nu_1 - \nu_2 = \nu_3 - \nu_4} \frac{([\mathbf{d}_1, \mathbf{h}_2]_x - [\mathbf{d}_2, \mathbf{h}_1]_x)([\mathbf{d}_3, \mathbf{h}_4]_x - [\mathbf{d}_4, \mathbf{h}_3]_x)}{\nu_1 \nu_3}$$
$$\times \frac{\sin^2 2\pi(\nu_1 - \nu_2)\tau}{\tau(2\pi(\nu_1 - \nu_2))^2} \cos 2\pi(\psi_1 - \psi_2 - \psi_3 + \psi_4)$$

where the first summation is extended over all combinations of indices (1) (2), each combination being counted once. In the second summation each term of the first summation is combined once with every other term. The first summation gives rise to the term taken into account by Fokker. In fact, the space average of $\overline{([\mathbf{d}_1, \mathbf{h}_2]_x - [\mathbf{d}_2, \mathbf{h}_1]_x)^2}$ is readily found to be $\frac{4}{9}(d^2)^2$.

Remembering that

$$\sum_{d\nu} d^2 = 2\rho d\nu,$$

and that

$$\int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2} dx = \pi,$$

it is found that the contribution of the first summation is

$$(\overline{\mathrm{X}^2/\tau})^1 = \frac{2}{9}\left(\frac{e^2}{4\pi mc}\right)^2 \int_0^\infty \frac{\rho^2}{\nu^2} d\nu. \quad . \quad . \quad . \quad . \quad . \quad (7')$$

Comparing the structure of formulæ (6) and (7), we see that the *phase terms, i. e.* terms depending on $\psi_1 - \psi_2 - \psi_3 + \psi_4$, are likely to contribute relatively as much to ϵ^2 and X^2/τ in comparison with the absolute terms (6′), (7′) if there is a grouping of waves so far as their direction of propagation is concerned.

We must remember here that the second term in (6) is extended over all such ν's that $\nu_1-\nu_2=\nu_3-\nu_4$, and also such that $\nu_1-\nu_3=\nu_2-\nu_4$. This means that contributions to the sum will be brought about not only by having (1, 2) and (3, 4) in the same groups, but also by having (1, 3), (2, 4) in the same groups; for with this condition $\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2$ is of the same sign as $\mathbf{d}_3\mathbf{d}_4+\mathbf{h}_3\mathbf{h}_4$ if polarization persists through each group. There is a very much greater number of possibilities of such combinations than of the groupings (1, 2) (3, 4), and we are thus tempted to consider these as the only essential groupings. From this point of view, the average value of

$$(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)(\mathbf{d}_3\mathbf{d}_4+\mathbf{h}_3\mathbf{h}_4)\left(\frac{\sin x_{12}}{x_{12}^3}-\frac{\cos x_{12}}{x_{12}^2}\right)\left(\frac{\sin x_{34}}{x_{34}^3}-\frac{\cos x_{34}}{x_{34}^2}\right)$$

is the same as that of

$$(\mathbf{d}_1\mathbf{d}_2+\mathbf{h}_1\mathbf{h}_2)\left(\frac{\sin x_{12}}{x_{12}^3}-\frac{\cos x_{12}}{x_{12}^2}\right)^2.$$

Quite similarly in (7) the average value of

$$([\mathbf{d}_1,\mathbf{h}_2]_x-[\mathbf{d}_2,\mathbf{h}_1]_x)([\mathbf{d}_3,\mathbf{h}_4]_x-[\mathbf{d}_4,\mathbf{h}_3]_x)\frac{\sin^2 2\pi(\nu_1-\nu_2)\tau}{\tau(2\pi(\nu_1-\nu_2))^2}$$

is the same as that of

$$([\mathbf{d}_1,\mathbf{h}_2]_x-[\mathbf{d}_2,\mathbf{h}_1]_x)^2\frac{\sin^2 2\pi(\nu_1-\nu_2)\tau}{\tau(2\pi(\nu_1-\nu_2))^2}.$$

It is thus seen that the ratios in which (6), (7) are changed by the presence of the second terms may be the same.

§ 4. We shall consider now the relation of the problem of the motion of a free electron in black body radiation to that of the motion of a Bohr atom in the same radiation as considered by Einstein * in 1917. We must first of all decide in how far a free electron may be considered to be the limiting case of an electron bound to a Bohr atom. Let the binding to the nucleus be quasi-elastic, so that the equation of motion is

$$m\ddot{x}-\frac{e^2}{6\pi c^3}\dddot{x}+m\omega_0^2x=e\left\{d_x+\frac{1}{c}[\mathbf{v},\mathbf{h}]_x\right\}.$$

Let us suppose temporarily that the term $\frac{1}{c}[\mathbf{v},\mathbf{h}]_x$ has a negligible effect. Let d_x be periodic and of frequency $\frac{\omega}{2\pi}$. Then the amplitude x of the vibration set up in x is

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* Einstein, *Phys. Zeit.* xviii. p. 121 (1917).

related to the amplitude $|d_x|$ of d_x by

$$|x|^2 = \frac{e\,|d_x|^2}{m^2(\omega_0^2-\omega^2)^2+\left(\frac{e^2}{6\pi c^3}\right)^2\omega^6} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If ω is near to the resonant value ω_0, the ratio of the second term in the denominator to the first is that of $\frac{\omega^4}{4m^2}\left(\frac{e^2}{6\pi c^3}\right)^2$ to $(\omega_0-\omega)^2$. The width of the band to which the oscillator responds is therefore proportional to ω^4, and is smaller for longer wave-lengths. Resonance for loosely-bound electrons is sharper than that of firmly-made Bohr atoms. We have therefore less reason for disregarding the effect of values of ω close to ω_0 in the case of loosely-bound electrons than we have in Einstein's case of 1917, and similarly we see more reason for taking into account values of $\omega\neq\omega_0$ in the case of firmly-built atoms than in Fokker's case.

The kinetic energy of a bound electron obtained from (8) and summed for all values of ω is in absolute value

$$\frac{m}{2}|\dot{x}|^2 = \frac{m}{2}\int_0^\infty \frac{\omega^2 e^2\,|d_x^2|_\omega\,d\omega}{m^2(\omega_0^2-\omega^2)^2+\left(\frac{e^2}{6\pi c^3}\right)^2\omega^6},$$

where the effective value of d_x^2 is taken.

The effect of frequencies in the neighbourhood of ω_0 is

$$\frac{m}{2}\int_0^\infty \frac{e^2\ d_x^2{}_\omega\,d\omega}{4m^2\left\{(\omega_0-\omega)^2+\frac{\omega^4}{4m^2}\left(\frac{e^2}{6\pi c^3}\right)^2\right\}} = \frac{3\pi^2c^3}{2}\,\frac{|d_x^2|_{\omega_0}}{\omega_0^2},$$

where $|d_x^2|_{\omega_0}$ is the sum of the effective squares of all the d_x in a range $\omega-\omega_0=1$. Relatively to the energy present the kinetic energy attained due to resonance is thus seen to be greater for small values of ω_0. (The Rayleigh-Jeans formula is, in fact, adjusted so as to make $|d_x^2|_{\omega_0}/\omega_0^2=\text{const.}$) Thus again we see no definite reason for treating loosely-bound electrons on a basis different from rigidly bound atoms, and even expect loosely-bound structures to accentuate properties of resonance on account of a lower frequency and a decreased loss of energy by radiation.

Since a strictly free electron is a physical impossibility, we could put the whole problem on the basis of Einstein's which we have already discussed [*]. This, however, would be unfair, because Einstein's problem of (1917) must be solved by taking into account other frequencies than those in the immediate neighbourhood of the emission line. This is indicated by the fact that matter has a refractive index for wave-lengths different from the emission wave-lengths, as well as by the possibility of thinking consistently of the motion of free electrons in which other frequencies than the natural $\nu=0$ are taken into account.

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[*] G. Breit, Phys. Rev. Oct. 1923, pp. 313–319.

As shown in § 2, the vibratory motion is very small, and from §§ 2, 3 it follows that the contribution to $\overline{X^2}/\tau$ of the radiation pressure-effects becomes very small when $\nu \doteq 0$. Thus free electrons may be thought of as the limiting case of bound electrons, the influence of frequencies outside the resonance band being in this case the more important. This can be shown to be the case by considering the radiation pressure-effects in the band and outside of it, the contribution in the band being found to vanish for infinitely loose binding on account of a small value of $\rho(\nu)$ for small ν.

It will be worth while to go into Einstein's case in slightly greater detail. Two states of the atom are considered: one of high energy ϵ_2, and another of low energy ϵ_1. A fall from ϵ_2 to ϵ_1 gives rise to the emission of $h\nu=\epsilon_2-\epsilon_1$. A rise from ϵ_1 to ϵ_2 gives rise to the absorption of the same quantum. The spontaneous probability of emission in the time *dt* is *a dt*, the probabilities of absorption and of emission due to radiation are $b_1^2\rho\, dt$ and $b_2'\rho\, dt$ respectively. The *a priori* probabilities of 1, 2 are p_1, p_2 respectively. For equilibrium

$$(a+b_{21}\rho)p_2 e^{-\frac{\epsilon_2}{kT}} = b_1^2\rho p_1 e^{-\frac{\epsilon_1}{kT}},$$

which leads to

$$\rho = \frac{\alpha\nu^3}{e^{\frac{h\nu}{kT}}-1},$$

where

$$\alpha\nu^3 = \frac{a}{b_2'}, \qquad b_1^2 p_1 = b_2' p_2.$$

In order that the Brownian movement should give a kinetic energy of kT/2 per degree of freedom, Einstein's equation

$$\frac{\overline{\Delta^2}}{\tau} = 2\mathrm{R}k\mathrm{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

must be satisfied. Here Δ is the momentum imparted to the atom in the time τ, and Rv is the systematic resisting force to an atom having the velocity v. The term a gives rise to transitions which in the quantum theory correspond to the dissipated energy of the classical case. It is for this reason that the correspondence principle relates a to the time constant of the classical theory. The amount of energy dissipated per second is then $p_2 e^{-\frac{\epsilon_2}{kT}} a h\nu$. If the atom moves with velocity v, the amount of momentum absorbed from the radiation is $\frac{v'}{c^2}$ times this energy where

$$v' = v\left(3 - \frac{\nu}{\rho}\frac{\partial\rho}{\nu}\right).$$

(See writer, *l. c.* Postulate 1.) Thus

$$\mathrm{R} = \left(3 - \frac{\nu}{\rho}\frac{\partial\rho}{\partial\nu}\right) p_2 e^{-\frac{\epsilon_2}{kT}} a \frac{h\nu}{c^2}. \quad . \quad . \quad . \quad (10)$$

Again, the average square of the fluctuation of energy is obtained by multiplying the number of transitions between (1), (2) by $h^2\nu^2$. This is per second $2p_1 e^{-\frac{\epsilon_1}{kT}} b_1{}^2 \rho (h\nu)^2$. If it is granted that this result must be divided by c^2 in order to obtain $\overline{\Delta^2}/\tau$ [See writer, *l. c.* Postulate 2. This condition is an expression of the statistical equivalence of **d** and **h** and of the physical existence of the force $\frac{e}{c}[\mathbf{v}, \mathbf{h}]$ alongside with $e\mathbf{d}$], we have then

$$\frac{\overline{\Delta^2}}{\tau} = 2p_1 b_1{}^2 e^{-\frac{\epsilon_1}{kT}} \rho \left(\frac{h\nu}{c}\right)^2. \quad . \quad . \quad . \quad . \quad (11)$$

Substituting (10), (11) into (9), it is found that (9) is satisfied if

$$\rho = \frac{\alpha\nu^3}{e^{h\nu/kT} - 1}.$$

The writer's postulates (1), (2) are thus sufficient conditions in order that (9) should be satisfied. Postulate (1) is identical with the supposition we have made in § 2 above as to the nature of Fokker's Q. Postulate (2) is less specific than the treatment of Fokker's $\overline{X^2}/\tau$ in §§ 2, 3. But both involve the same idea: viz., the agitating influence is the force $\frac{e}{c}[\mathbf{v}, \mathbf{h}]$ which acts simultaneously with the force $e\mathbf{d}$. In the case of free electrons the transitions in the motion are gradual, and the calculation of both the absorbed energy and the absorbed momentum is manageable by the classical theory. In the case of a quantized atom the motion changes discontinuously. When the motion changes from the state (1) to the state (2), we assign a greater energy to the atom. Our postulate (2) has then the meaning that if the absorption of energy should be pictured as work done on a resonator, and if simultaneously the amount of transferred momentum due to $\frac{e}{c}[\mathbf{v}, \mathbf{h}]$ should be computed, then this momentum may be assigned to the atom simultaneously with the assignment of the absorbed energy. This momentum is not necessarily $\frac{h\nu}{c}$. The statistical effect of this momentum is, however, the same as that of Einstein's needle quanta. So far both problems may be thought of in terms of the force equation

$$\mathbf{F} = \mathbf{d} + \frac{1}{c}[\mathbf{v}, \mathbf{h}],$$

where it is remembered that a certain amount of work must be done by the force before the atom changes from 1 to 2.

§ 5. One of the fundamental objections to classical electrodynamics is its apparent inability to explain the large accumulation of energy which is necessary for the absorption of a quantum in experiments on the photoelectric effect. The amount of energy carried by a plane wave across an area of atomic dimensions is calculated, and is found to be too small to give a quantum in a reasonable length of time *. It does not seem to the writer that a calculation of this sort is capable of deciding what the absorbed energy may be. In fact, on the classical theory the quantity which is spoken of as absorbed energy is *force times distance* where the force is $e\mathbf{d} + \frac{e}{c}[\mathbf{v}, \mathbf{h}]$, and the distance is the distance travelled by the charge on which the force is exerted. The theorem of conservation of energy on classical electrodynamics is devised in such a way as to account for the absorbed energy by means of quantities connected with the field. It states that the energy absorbed by matter is absorbed at the expense of the energy stored in space (or æther) and the flux of Poynting's vector into the space. The energy flowing across a section of a plane wave in the absence of an atom has thus little to do with the amount of energy which may be absorbed by an atom when placed into the wave.

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* Millikan, 'The Electron,' p. 232 (Univ. of Chicago Press, 1916). See also reference to Lord Rayleigh's criticism, Phil. Mag. xxxii. p. 188 (1916).

On the classical theory, a charge the motion of which is confined to a small region may absorb from a plane wave an amount of energy which is great in comparison with the energy flowing over the region due to the wave in the absence of the charge. All that is necessary for this is a properly controlled vigorous motion of the charge which keeps its velocity in phase with and parallel to the electric vector of the wave. Inside a surface just enclosing the region to which the charge is confined there is not enough field energy to supply the demand of the theorem of conservation, but this amount is automatically satisfied by the flux of Poynting's vector through the surface. The essential addition to the field of the wave is the magnetic field due to the moving charge. This gives rise to a term in Poynting's vector which, when integrated over the surface, gives a flux contributing the main part of the necessary energy.

We must next decide what element in the atom and what characteristics of its motion we should consider in order to compute the energy absorbed. Bohr's principle of correspondence is of fundamental importance in this connexion, for it indicates the manner in which the classical radiation force $\frac{e^2}{6\pi c^3}\ddot{v}$ finds expression in the quantum theory. This radiation force is neglected in the formulation of quantum conditions. However, the sin committed by forgetting it is punished by the failure of the atom to conform to quantum rules rigidly. The atom has a spontaneous tendency, given by Einstein's $A_m{}^n$ (our symbol *a* of the preceding §), to fall from a high energy state to a low one; and this tendency is such that on the average the emission of energy from a set of atoms put into Einstein's state *n* may be likened so far as the frequency and the intensity of the radiation are concerned to the radiation from a set of "corresponding" classical mechanisms, these being essentially constant frequency vibrators having in their motion a close similarity to the mean motion of the electron between the two states *m*, *n*. So far as frequency is concerned, the analogy is exact (Bohr's correspondence theorem). So far as intensities go, the analogy or another similar analogy is probably exact also (Bohr's correspondence principle). Now, the amount of energy radiated may be thought of as the amount of energy dissipated in the motion of the atom owing to the action of the radiation force $\frac{e^2}{6\pi c^3}\ddot{v}$. This force may be thus thought of as exerting a cumulative effect on the equivalent corresponding resonator. When the accumulated dissipated energy acquires the value $h\nu$, the atom jumps from m to n. The force $\frac{e^3}{6\pi c^3}\ddot{r}$ is a stranger to the quantum conditions. It affects them only inasmuch as it makes strictly periodic motions impossible, except in quantum orbits of lowest energy, and the width of spectral lines may be thought of by formal quantum theory when violations in the simple periodicity due to the quantum jumps are considered*. Similarly, the force due to the exciting wave is a stranger to quantum conditions, and its action is similarly cumulative. The wave can be thus thought of as doing work on the "corresponding vibrator." If the frequency of the wave is equal to the frequency of the vibrator (neglecting the broadening of that frequency due to the action of $\frac{e^2}{6\pi c^3}\ddot{r}$), work will be done at a steady rate, and ultimately a quantum $h\nu$ will be absorbed. Then the atom leaves the state n and goes into the state m. Similarly, while it is in the state of high energy m, the phase of the wave may turn out to be such that the wave does a negative amount of work ($=-h\nu$) on the atom (or perhaps this, together with $\frac{e^2}{6\pi c^3}\ddot{r}$, does that work). As a result, a jump from n to m takes place. It is seen, therefore, that a fairly concrete explanation of the correspondence principle and of the position of absorption bands of a substance may be obtained by the introduction of the *corresponding vibrators* together with a consideration of the effects of $\frac{e^2}{6\pi c^3}\ddot{r}$. The quantitative side of the absolute coefficients of absorption has been discussed by Ladenburg and Reiche, and by Milne †. Their discussions, however, are based on a formal appeal to the principle of correspondence and do not depend on the mechanism just proposed.

In calculation of the photoelectric effect, our picture can be used only if there is sufficient possibility for the absorption of a quantum. The amount of energy absorbed per unit time from a wave having an electric intensity of amplitude d, a frequency ν, and in exact synchronism with the vibrator, is then $\pi e d A \nu$, where A is the amplitude of the vibrator. This amplitude we relate to the amplitude of the electronic motions, and we suppose that it is the same as the amplitude which must be considered for emission. For our present purpose we need to know only the order of magnitude of the amplitude, and we may take it to be the radius of the electronic orbit. The value of d involves some uncertainty. Let us suppose that we are dealing with a monochromatic wave emitted by a flame sending out N quanta per second. If we should calculate on the old viewpoint the amount of energy flowing per second through an area of atomic dimensions at a distance of r cm. from the source that energy would be $\frac{N\,h\nu}{4\pi r^2}\pi a^2$, where a is the atomic radius. The number of quanta sent through per second is then $Na^2/(4r^2)$. With

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* G. Breit, Proc. Nat. Acad. ix. no. 7, pp. 244–246 (July 1923).
Added in proof. For similar considerations, see Tolman, Phys. Rev. p. 693, June 1924. Ehrenfest and Tolman, Phys. Rev. p. 287, Sept. 1924.

† Ladenburg and Reiche, *Naturwissenschaften*, xi. p. 584 (July 1923). Milne, Phil. Mag. xlvii. p. 209 (1924). Ladenburg, *Zeitsch. f. Phys.* iv. p. 451 (1921).

$$N = 10^{14}, \quad a = 10^{-8} \text{ cm.}, \quad r = 100 \text{ cm.},$$

this is $2{\cdot}5 \times 10^{-7}$. Thus one must wait 4×10^6 sec. before a quantum is absorbed on the view that Poynting's flux of the original plane wave accounts for the absorption. A quite different result is obtained if we adopt the view of work done on the equivalent resonator.

Let the time of emission of each quantum be τ (length of wave train $=c\tau$). Using electrostatic units and letting

$$d = E_0 \cos \omega t,$$

the value of E_0 is determined by

$$4\pi r^2 \frac{1}{8\pi} E_0^2 c\tau = h\nu.$$

During the interval τ there are $N\tau$ wave trains emitted. Provisionally we may assume that the phases of these are random. The resultant value of E_0^2 is then given by

$$E_0^2 = \frac{2N}{r^2}\frac{h\nu}{c}.$$

The number of quanta absorbed which could be absorbed per second if the absorption should go on at the maximum rate is then

$$ae\frac{\pi\nu}{h\nu}\sqrt{\frac{2N\,h\nu}{r^2 c}} = \frac{\pi a e}{r}\sqrt{\frac{2N\nu}{ch}},$$

with

$$a = 10^{-8} \text{ cm.}, \quad r = 10^2 \text{ cm.}, \quad N = 10^{14}, \quad \nu = 10^{15}/\text{sec.};$$

this gives 5×10^3. Thus an atom must wait only $0{\cdot}0002$ sec.

before a sufficient amount of work has been done. Between the old view and the one here presented we see thus a divergence by a factor 2×10^{10} *.

Even though the view presented here is numerically very much more satisfactory than that previously held, the estimate of time which we just made is likely to be too high. One reason for this is the possibility of interference actions in the wave front such as has been suggested by Lorentz. The other is the purely theoretical possibility of cumulative actions due to previous influence on the atom. For we are computing essentially the storing of energy due to work done on the equivalent oscillator, and we must admit the possibility of this storing being cumulative in the sense that atoms which have been exposed previously and which have stored some energy need a smaller additional amount. From this point of view our calculation applies to fresh atoms only.

Even though we attempt above to look at absorption as related to the classical absorption, we do not wish to imply that the phenomenon is a classical one. All experimental evidence points to the opposite conclusion, viz. that there are transitions between discrete states. The probability of these transitions, however, is calculable on a classical basis, as pointed out above. This view is similar to that of Mie †. It is an extension of the principle of correspondence to the case of absorption, provided the principle of correspondence is formulated in terms of the force $\frac{2e^2}{3c^3}\dddot{x}$.

The exact manner in which external influences are to be considered as acting on the equivalent resonator is, of course, uncertain. That some such action exists, however, appears to be indicated by various phenomena. Anomalous dispersion apparently has no other possible explanation than that of an interaction between the incident wave and the equivalent resonator. It is of interest to observe in this connexion that as long as the frequency ν of the incident wave is different from the frequency ν_0 of the equivalent oscillator (supposed here for simplicity infinitely sharp), there is no experimental indication of a true change in the quantum

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* The order of magnitude of Lord Rayleigh's correction is 10^6. The γ-ray difficulty cited by Millikan is not necessarily real, because the electrons absorbing γ-rays may be much more rapidly moving than the optical ones.

† G. Mie, *Ann. der Physik*, lxxiii. p. 195 (1924).

state of the atom. This may be interpreted in two ways: (*a*) the work done on the equivalent resonator by the incident wave is never comparable to $h\nu$ if $\nu-\nu_0\neq 0$; (*b*) the transitions between levels the energy difference of which is given by $\Delta W = h\nu_0$ cannot be caused by values of $\nu\neq\nu_0$ (disregarding, for the present, diffuseness of quantization). Which of these hypotheses is true is very hard to answer. However, it appears that (*a*) is likely to be the case. In fact, let the motion of the oscillator be given by

$$x = A\sin 2\pi\nu_0 t,$$

and let the x component of the electric intensity of the incident wave be $E_0\cos(2\pi\nu t-\psi)$. The amount of work done by the wave between the instants t_1, t_2 is then

$$\tfrac{1}{2}E_0 e\nu_0 A\left[\frac{\sin(2\pi(\nu-\nu_0)t-\psi)}{\nu-\nu_0}+\frac{\sin(2\pi(\nu+\nu_0)t-\psi)}{\nu+\nu_0}\right]_{t_1}^{t_2}.$$

Only the first term in this expression is of importance. The maximum value of absorbed energy due to it is $\dfrac{E_0 e\nu_0 A}{2(\nu-\nu_0)}$. In order that this term should be appreciable in comparison with the action of a wave for which $\nu=\nu_0$ acting for a time τ, we must have $\dfrac{1}{\nu-\nu_0}$ comparable to τ. For the time τ we may take the time corresponding to the length of a wave train, and thus corresponding according to the measurements of Wien * and numerous other evidences to the time constant on the classical theory. We shall show presently, however, that $\dfrac{1}{\nu-\nu_0}$ is comparable to τ only if the frequency ν is within the width of the emission line ν_0. We see, therefore, that as long as resonance is sharp, we need not be concerned with a differentiation of the possibilities (*a*), (*b*).

The property of $\dfrac{1}{\nu-\nu_0}$ in relation to τ which we have just used is related to some general properties of oscillators which are conveniently kept in mind in connexion with the subject here discussed. These properties are expressed by the mathematical identities

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* W. Wien, *Ann. der Physik*, lxxiii. p. 483 (1924).

$$2\tau_0\tau_1\int_{-\infty}^{+\infty}\frac{d\nu}{[1+(2\pi(\nu-\nu_0)\tau_0)^2][1+(2\pi(\nu-\nu_1)\tau_1)^2]}$$

$$=\frac{\frac{\tau_0\tau_1}{\tau_0+\tau_1}}{1+\left(2\pi(\nu_1-\nu_0)\frac{\tau_0\tau_1}{\tau_0+\tau_1}\right)^2}, \quad \text{(I.)}$$

$$\int_{-\infty}^{+\infty}\frac{\cos(2\pi\nu t)}{1+(2\pi(\nu-\nu_0)\tau)^2}d\nu=\frac{e^{-\left|\frac{t}{\tau}\right|}}{2\tau}\cos(2\pi\nu_0 t), \quad . \quad \text{(II.)}$$

$$\int_{-\infty}^{+\infty}\frac{(2\pi(\nu-\nu_0)\tau)\sin(2\pi\nu t)}{1+(2\pi(\nu-\nu_0)\tau)^2}d\nu$$

$$=\frac{e^{-\left|\frac{t}{\tau}\right|}}{2\tau}\frac{|t|}{t}\cos(2\pi\nu_0 t). \quad \text{(III.)}$$

Formulas (II.), (III.) show that a damped wave beginning at $t=0$ and having the time constant τ (represented by $\frac{1}{2\tau}e^{-\left|\frac{t}{\tau}\right|}(1+|t|/t)\cos(2\pi\nu_0)t))$ may be thought of as the sum of the two Fourier integrals on the left-hand sides of (II.), (III.). Adding (II.), (III.), we have

$$\int_{-\infty}^{+\infty}\frac{\cos(2\pi\nu t-\tan^{-1})(2\pi(\nu-\nu_0)\tau)}{\sqrt{1+(2\pi(\nu-\nu_0)\tau)^2}}d\nu$$

$$=\frac{e^{-\left|\frac{t}{\tau}\right|}}{2\tau}(1+|t|/t)\cos(2\pi\nu_0 t). \quad \text{(IV.)}$$

The main contributions to the integral on the left come from a band of frequencies determined by such values of ν that $2\pi(\nu-\nu_0)\tau$ is not too great in comparison with unity. This shows that the band of frequencies which would be emitted by an oscillator would be confined to a region in which the time $\frac{1}{\nu-\nu_0}$ is not too small in comparison with τ.

Again, the motion of the oscillator is given by

$$\ddot{x}+\kappa\dot{x}+(2\pi\nu_0)^2x=\frac{E_t e}{m}, \quad . \quad . \quad . \quad . \quad . \quad \text{(V.)}$$

where ν_0 is the natural frequency, κ the dissipation factor given by $\kappa = \frac{2}{3}\frac{e^2}{c^3}(2\pi\nu)^2$ on the electrostatic system of units. The time constant $\tau = \frac{2}{\kappa}$. If E_x is of the form $E_{x0}\cos(2\pi\nu t - \psi)$, the absolute value of the forced vibration in x is given by

$$|x = \frac{E_x | e/m}{\sqrt{(2\pi\kappa\nu)^2 + (2\pi)^4(\nu_0{}^2 - \nu^2)^2}} \quad . \quad . \quad . \quad \text{(VI.)}$$

It is easily seen that the expression under the radical of this formula is very nearly $(2\pi\kappa\nu)^2[1 + (2\pi(\nu - \nu_0)\tau)^2]$. Thus forced vibrations have an appreciable value only if the time $\frac{1}{\nu - \nu_0}$ is not too great in comparison with the time constant τ[*].

Further, according to equation (I.) the effect of a damped wave (IV.) having the time constant τ_0 and a natural frequency ν_0 on a resonator having a time constant τ_1 and a natural frequency ν_1 depends on $\nu_1 - \nu_0$ in such a way as though the resonator were undamped and the wave had a small time constant

$$\left(\frac{1}{\tau_0} + \frac{1}{\tau_1}\right)^{-1} = \frac{\tau\tau_1}{\tau_0 + \tau_1},$$

or otherwise in such a way as though the wave were undamped and the resonator had a time constant $\frac{\tau_0\tau_1}{\tau_0 + \tau_1}$. (The Bjerknes decrement law[†].)

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[*] It is of interest to note that to within the approximation here considered, the amplitude induced in a resonator by a wave of frequency ν and given by (VI.) is proportional to the amplitude of the component oscillation in the Fourier integral (IV.). This means that the width and the spectral distribution of the band of frequencies from which the resonator absorbs energy is the same as the width of the bands into which it radiates. If it were not for this fact there could be no true equilibrium of a resonator with black body radiation.

[†] From (1.) we obtain the following results:—

(*a*) We have:

$$(2\tau_0)^2\tau_1{}^2\int_{-\infty}^{+\infty}\frac{d\nu}{[1+(2\pi(\nu-\nu_0)\tau_0)^2][1+(2\pi(\nu-\nu_1)\tau_1)^2]}$$

$$= 2(\tau_0+\tau_1)\frac{\left(\frac{\tau_0\tau_1}{\tau_0+\tau_1}\right)}{1+\left(2\pi(\nu_0-\nu_1)\frac{\tau_0\tau_1}{\tau_0+\tau_1}\right)^2}:$$

This we interpret by saying that an oscillator having a time constant τ_0, when subjected to a group of damped wave trains recurring periodically at intervals of 1 second having a peak amplitude 2 and a time constant τ_0 (see (IV.)), acquires an average energy which is $2(\tau_0+\tau_1)$ times the

These resonance relations, which are of importance in wireless telegraphy, are known to be true experimentally, and it is natural to require an extension of these relations in the quantum theory of spectral lines. Equation (IV.) appears to be the natural viewpoint to take in the quantum

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energy which would be acquired by a resonator having the same mass and restitution constant, but a decreased time constant $\tau' = \frac{\tau_0\tau_1}{\tau_0+\tau_1}$ if this resonator were exposed to a monochromatic wave of frequency ν, and of unit amplitude.

(*b*) We have:

$$(2\tau_0)^2\tau_1\int_{-\infty}^{+\infty}\frac{d\nu}{[1+(2\pi(\nu-\nu_0)\tau_0)^2][1+(2\pi(\nu-\nu_1)\tau_1)^2]}$$

$$= 2\tau_0\,\frac{\frac{\tau_0\tau_1}{\tau_0+\tau_1}}{1+\left(2\pi(\nu_1-\nu_0)\frac{\tau_0\tau_1}{\tau_0+\tau_1}\right)^2}.$$

This means that the energy dissipated by an oscillator having a time constant τ_1 from a group of waves having a time constant τ_0, recurring periodically at intervals of 1 sec. and having a peak amplitude 2, is $2\tau_0$ times the energy which would be dissipated by an oscillator having a time constant $\frac{\tau_0\tau_1}{\tau_0+\tau_1}$ (with mass and restitution constants unchanged) from a monochromatic wave of frequency ν_1 and unit amplitude.

The right-hand side of the above equation may be re-written as

$$\frac{1}{2}\,\frac{\tau_0+\tau_1}{\tau_1}\,\frac{\left(\frac{2\tau_0\tau_1}{\tau_0+\tau_1}\right)^2}{1+\left(2\pi(\nu_1-\nu_0)\frac{\tau_0\tau_1}{\tau_0+\tau_1}\right)^2}.$$

Since

$$\int_{-\infty}^{+\infty}\frac{\tau_2\,d\nu}{1+(2\pi(\nu-\nu_1)\tau_2)^2}=\tfrac{1}{2},$$

we can state that the energy dissipated may be also thought of as that dissipated from a group of damped waves with a time constant $\frac{\tau_0\tau_1}{\tau_0+\tau_1}$ having unit group frequency, a peak amplitude of 2, a frequency ν_0, and acting on a very sharp resonator with a very large time constant τ_2, provided that energy is multiplied by $\frac{(\tau_0+\tau_1)}{\tau_1}$.

As special cases from (*b*) we obtain

(*b*′) The energy dissipated by an infinitely sharp resonator from a group of waves having a peak amplitude 2, a group frequency 1, and a time constant τ_0 is $2\tau_0$ times the energy dissipated from a monochromatic wave train of unit amplitude, of frequency ν_0, by a resonator having a time constant τ_0.

theory. A damped wave is resolved by this equation in a Fourier integral. The expansion happens to be of such a nature as to be similar to (VI.) integrated over ν. It appears natural to require the same similarity in the quantum case. Further, if the physical information of equation (I.) (the reciprocity of τ_0, τ_1) may be legitimately extended to the quantum case, then it appears that one must either form a dynamical model leading ultimately to spectral distributions equivalent to (IV.) or else one must postulate the direct applicability of (I.).

It is natural to look for a quantum-theory analogue of (I.), because the simplest fundamental phenomenon is the transition of one atom from a state of high energy to one of low followed by a transition of another atom in the reverse direction. The first phase leads to the emission of a quantum having a finite length of emission, and therefore the general characteristics of (IV.). The second phase is the absorption of that quantum. This we may suppose to happen in a manner analogous to (I.). If such is the case, we should expect that experiments on the absorption of resonance radiation will give apparently larger width of spectral lines than one should suppose from the value of τ. If the emitting and absorbing atoms have the same τ_0, the effective value of τ is $\tau_0/2$.

The writer knows of no direct experimental evidence bearing on the existence of such effects. However, by analogy with classical theory it would be surprising if they were absent, and further it would be very difficult to see how equilibrium with black body radiation is maintained unless the emission and absorption bands have the same width and spectral distribution. The formulation of quantum theory does not seem satisfying therefore before one is able to account for the width of lines for emission as well as absorption on the same basis. A tentative theory explaining the width due to collisions on the same basis as the intrinsic width has been given by the writer (Proc. Nat. Acad. *l. c.*). A different and in all probability more correct point of view is taken by Bohr *, who ascribes the width of lines to an intrinsic inaccuracy in the applicability of quantum rules which causes the spectral width. Whether the broadening is actual as suggested by Bohr, or statistical as the above would suggest, the order of magnitude of the effect is such as would be caused on a classical resonator damped by the force $\frac{2}{3}\frac{e^2}{c^3}\ddot{v}$, or else undamped but interrupted by external influences at time intervals comparable with the time constant of the damped resonator*. Thus here also there is a certain similarity of the action of the $\frac{2}{3}\frac{e^2}{c^3}\ddot{v}$ and of the external forces. To summarize:

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* *Zeits. f. Phys.* xiii. pp. 145-153.

(1) The equations of motion of an electron in its orbit are to a first approximation classical, provided the radiation force $\frac{2}{3}\frac{e^2}{c^3}\ddot{v}$ and the wave force $e\mathbf{d}+\frac{e}{c}[\mathbf{vh}]$ are disregarded.

(2) The electron leaves its quantized state and passes into a state of higher or lower energy if the amount of work done on it by either of the neglected forces is equal to the energy difference between these states (or perhaps both). The forces are regarded as acting on a collection of equivalent resonators which represent the mean motions of the electron between various quantized states.

(3) Besides the function of determining probabilities of transitions between quantum states, each of the equivalent resonators of frequency ν_0 acts on incident wave of frequency ν as though it were a classical resonator. This view is forced on us by phenomena of dispersion†.

The writer's purpose in sketching the above theory is to point out that the classical wave theory, if given proper attention, is not powerless in dealing with phenomena for which light-quanta have been especially devised. He may be permitted to call attention to a phenomenon (in addition to those of interference and diffraction which are strongly emphasized by Bohr) which apparently is in favour of classical wave theory. This is the tendency of a γ-ray to emit β-rays out of the atom in which the γ-ray is produced. The inapplicability of light-darts is mentioned by Meitner[*]. It is of interest to point out that on the wave theory, estimating the time of emission of the γ-rays by the classical formula, a value of the electric intensity in the neighbourhood of the K ring results which is comparable with the electrostatic field due to the nucleus. It seems very natural from the point of view of the wave theory that the electron is thrown out under these circumstances. The evidence from the Compton effect at the present time is not very decisive, especially on account of a possible classical Doppler effect which is pointed out by Bauer[†]. It will suffice to state that the original Compton effect was diffuse; that the tertiary radiation effect of Duane, Clark, and Stifler is also diffuse; but that the lines photographed by J. A. Becker, E. C. Watson, W. R. Smythe, R. B. Brode, and L. M. Mott-Smith are sharp[‡].

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* The question as to a possible difference in the width of an emission and an absorption line, which has been discussed in the above-mentioned note, must apparently be answered in the sense that such a difference does not exist, for otherwise the equilibrium with black body radiation would not be maintained. This is true even in such radiation fields in which the atom rests in the lowest state a very long time before passing to an upper level.

† One can state this definitely only for frequency ν not too far from ν_0. However, in a purely speculative manner one might suppose that the deviation of atomic dynamics from classical is due to an interaction between electrons taking place in terms of equivalent resonators rather than according to the inverse square law.

After writing the article the writer received the May number of the 'Philosophical Magazine,' in which Bohr, Kramers, and Slater deal with the "virtual" resonators in connexion with optical phenomena in general. In many respects the views proposed here are similar to theirs. The aspects of the reactions discussed are different, however. The writer is very grateful to Prof. J. H. Van Vleck for many valuable comments.

The University of Minnesota,
June 3rd, 1924.

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[*] L. Meitner, *Zeits. f. Phys.* xix. p. 307 (1923); C. D. Ellis, *ibid.* x. p. 203 (1922), and Proc. Camb. Phil. Soc. xxvi. p. 274 (1922); L. Meitner, *Zeits. f. Phys.* xi. p. 35 (1922).

[†] E. Bauer, *C. Rend.* clxxvii. pp. 1031-1033 (1923).

[‡] American Physical Society, Washington Meeting, April 25-26.

Added in proof.—At the Washington Meeting of the American Physical Society (Dec. 1924) an apparently definite verdict in favour of the Compton effect has been obtained. As stated, however, this does not contradict the views presented.

LX. *The Mobility of the Positive Ions in Air.*

By H. B. Wahlin[*].

RECENT determinations of ionic mobilities have shown that the nature of the ions formed when a gas is ionized by α particles is more complex than was hitherto supposed to be the case. Erikson[†], using a modification of the air-stream method for determining mobilities, has demonstrated the existence in air of positive ions having mobilities of 1·35 and 1·89 cm./sec./volt/cm. The higher value was obtained if the mobility was determined soon after the ions were formed, and the lower value if the ions were allowed to remain in the gas for about ·5 sec. before the measurements were made. This lower mobility may be termed the normal mobility, since it represents the value for the most stable form of the ion after it has remained in the gas for an appreciable length of time. It is the value generally ascribed to the positive ion in air.

The most obvious explanation of Erikson's results is that the initial ion when aged picks up one or more neutral molecules to form a heavier ion, and therefore one with a lower mobility.

Nolan[‡], using the alternating field method as well as the air-stream method, has been able to obtain not only the values given above, but values much higher than those observed by Erikson. He found mobilities as high as 11·2 cm./sec./volt/cm. for the positive ion.

The work presented herewith was undertaken to determine if ions having mobilities lower than the value ascribed to the normal ion could exist in air. The method used was the Franck modification of the Rutherford alternating current method, and has been described in an earlier paper[§]. The ions were produced in an auxiliary chamber and were driven through a gauze by a field which could be varied from 2/10 volts/cm. to 39 volts/cm. The polonium used as an α particle source was so arranged that the ions had to pass through an appreciable layer of the unionized gas before passing through the gauze into the alternating field. Thus, by using a low auxiliary field, all the ions could be aged for a longer time than would be the case if the entire space in the auxiliary chamber were under the influence of the ionizing radiation. In this case an appreciable number of the unaged ions would pass into the alternating field even if the auxiliary field were so low as to allow the greater portion of the ions to become aged. The effect of such a condition would be to cause the mobility curves to approach the voltage axis less sharply, and consequently make a determination of the mobility from the intercept inaccurate.

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[*] Communicated by the Author.

[†] Erikson, H. A., Phys. Rev. n. s. xx., Aug. 1922.

[‡] Nolan, J. J., Proc. Irish Roy. Acad. xxxvi. A (1923).

[§] Wahlin, H. B., Phys. Rev. Sept. 1922.

The alternating field used in these determinations was obtained from the 60 cycle alternating current lighting circuit, and also from a vacuum-tube oscillator of the Hartley type. The frequency of this oscillator could be varied from 180 cycles/sec. to as high a value as was desired. When the oscillator was used, the alternating potential was obtained by grounding one side of the condenser in the oscillating circuit, and connecting the other side through the necessary key to the gauze. The alternating potential could then be varied by adjusting the plate voltage only.

Since the ions can age after passing through the gauze as well as before, it is necessary that the alternating field be as high as possible so that the ions will reach the collecting plate in a time short compared with the time necessary for ageing to take place. For this reason, the mobilities were determined in as high fields as could be measured accurately.

The air used in these determinations was dried by passing it slowly through a tube 75 cm. long filled with potassium hydroxide, then through a similar tube filled with calcium chloride, through two tubes of the same length containing phosphorus pentoxide, and finally through a trap cooled with liquid air, and a coil also immersed in liquid air. From this coil it passed into the measuring chamber. Water vapour as well as any other condensable vapours would thus be reduced to a minimum. The coil was in direct connexion with the chamber, and was therefore kept immersed in liquid air during a series of determinations.

Mobilities were determined with alternating fields ranging from 45 volts/cm. to 105 volts/cm., and with auxiliary fields as given above. The method of procedure was the usual one of measuring the charge received by the collecting plate in a given time for different values of the alternating potential. This charge can be taken as a measure of the current. From the data thus obtained a curve of the current against alternating voltages is plotted, and the mobility determined from this.

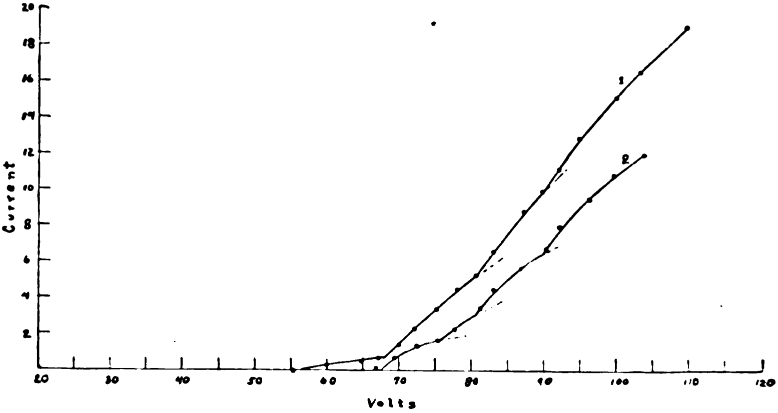
If only one type of ion were present, one would expect a smooth curve which would approach the voltage axis quite sharply. If more than one type of ion, each with a different mobility, were present, however, these curves would show quite sharp breaks. The resultant curve would in this case consist of a number of mobility curves each with a definite voltage intercept superimposed on a curve with a lower intercept. Therefore, from the breaks in the mobility curves as well as from the intercepts the mobility K may be determined by the relation

$$K = \frac{\pi n d^2}{\sqrt{2}V} \frac{P}{760},$$

where d is the distance between gauze and collecting plate, n is the frequency, V is the effective value of the alternating voltage, and P is the pressure in mm.

Fig. 1 illustrates the types of curves obtained at a pressure of 200 mm. with a distance d equal to 15·5 mm., and with

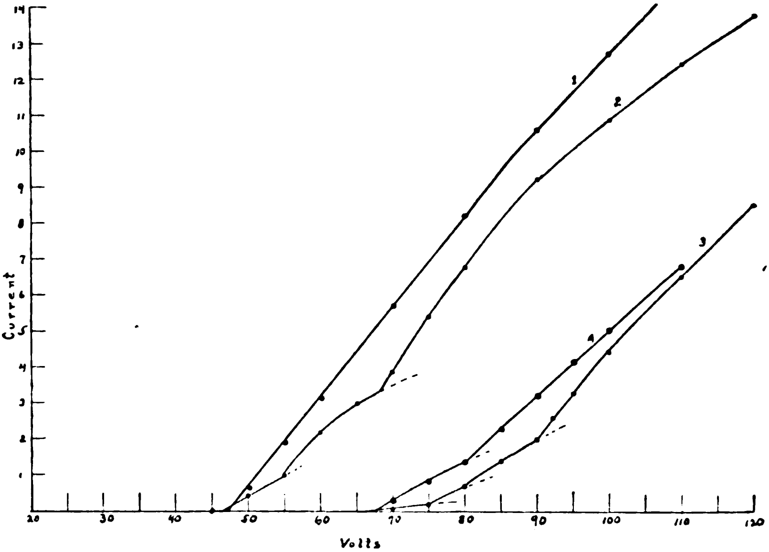
Fig. 1.



a frequency of 60 cycles/sec. Curve 1 was obtained with an auxiliary field of 3 volts/cm., and curve 2 with a field of 1·5 volts/cm. The curves shown in fig. 2 were obtained at a pressure of 50 mm. with a frequency of 230 cycles/sec., and with d = 15·5 mm. Curve 1 was obtained with an auxiliary field of 37·5 volts/cm., curve 2 with a field of 18 volts/cm., curve 3 with a field of 25/100 volts/cm., and curve 4 with a field of 1·5. The breaks appearing between 65 and 68 volts give the normal mobility 1·35 cm./sec./volt/cm. Breaks above this would correspond to lower mobilities and those below this to higher mobilities.

As may be seen from an examination of these curves, with sufficiently low auxiliary fields, *i. e.*, when the ions have a long time in which to age, the ions become more complex. Curve 1, fig. 2, shows that the initial ion is of one class only. It is possible that the initial ion observed here is a single molecule, and that the ageing consists in adding molecules or atoms to this. This, however, is not in accord with the work of Nolan, since he was able to observe ions with mobilities as high as 11·2 cm./sec./volt/cm., while the highest value observed in this work was 1·89 cm./sec./volt/cm. If this 1·89 ion corresponds to a single molecule ion, it would be difficult to account for the higher values obtained by Nolan. The writer was unable to observe the high mobilities given by Nolan. However, it is possible that these age so rapidly that unless they are caught immediately after formation they will pass over into a less mobile type. If that is the case, the experimental conditions were not favourable for the observation of them.

Fig. 2.



In some cases there were indications of a break in curve 3, fig. 2, and curve 2, fig. 1, at about 105 volts. This break could not be repeated at will, however, so that the mobility computed from this point was not noted.

The mobilities observed by the writer, together with the corresponding values found by Erikson and Nolan, are given below:—

Nolan	1·79	1·52	1·37			
Erikson	1·89	...	1 35			
Wahlin	1 89	1·57	1 35	1·20	1·10	·970

By an examination of the curves it may be seen that the 1·2 ion (intercept at 75 volts) disappears, as the ageing time is decreased, before the 1·10 ion. The explanation immediately suggests itself that this ion is due to a breaking down of the 1·10 ion. Possibly what happens is that the 1·35 ion adds on a molecule to form the 1·10 ion, and this loses an atom and forms the 1·2 ion.

The indications are therefore, that, while with average time of ageing the bulk of the ions present are such as to give a mobility of 1·35 cm./sec./volt/cm., with sufficient ageing ions with lower mobilities may be present. That the presence of these ions depends on the time of ageing is shown by the fact that the lower mobilities disappear as the ageing time is decreased, until finally those ions having a mobility of 1·89 cm./sec./volt/cm. predominate.

In conclusion the writer wishes to express his thanks to Mr. C. M. Bardin for his assistance in obtaining these data.

University of Wisconsin,
Madison, Wisconsin.
October 17, 1924.

LXI. *A Theorem in Tidal Dynamics.* *By* J. PROUDMAN (*Tidal Institute, University of Liverpool*) [*].

1. CERTAIN theorems on pairs of solutions of the wave-equation $(\nabla^2+\kappa^2)\phi=0$, of which Green's theorem is the root, are well known [†]. In the present paper [‡] these theorems are extended to the general dynamical equations of the tides.

Theorems of the type indicated appear likely to be helpful in the attempt to determine the characteristics of the actual tides far away from land. For example, if the tidal elevation is known at all points of the coast of a landlocked sea or ocean, the present methods provide a means of calculating the elevation at any point not on the coast. But the methods are not restricted to landlocked basins, as will be seen from §§ 5, 6.

The main theorem of the paper (§ 3) is a relation between certain integrals involving functions which satisfy the tidal equations, and also auxiliary functions which satisfy equations similar to, but not identical with, the tidal equations. The auxiliary functions contain a large arbitrary element and are not subject to any boundary conditions.

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[*] Communicated by the Author.

[†] See for example, Lamb, 'Hydrodynamics,' Arts. 290, 305.

[‡] Part of Adams Prize Essay, 1923.

Their determination is therefore free from the chief difficulty of tidal problems. For any distribution of ocean-depth they can be constructed by direct computational methods, and if the depth may be regarded as uniform they can be represented with great ease (§§ 5, 6).

2. *General Equations of the Tides.*

We shall denote by :

a	the radius of the Earth,
Ω	the angular speed of the Earth's rotation on its axis,
g	the acceleration due to gravity,
θ, χ	the co-latitude and east longitude of any point,
x, y	Cartesian coordinates in the mean surface of a flat sea,
h	the depth of water below any point of the mean surface,
t	the time,
ζ	the elevation of the free surface of the water at any time above any point of the mean surface,
u, v, ν	the mean values along any vertical of the velocity-components at any time in the horizontal directions of increasing θ, χ or x, y, and along the normal to a section respectively,
$-g\bar{\zeta}$	the potential of the astronomical disturbing forces,
F, G	the components of the external frictional force per horizontal area and per density of the water,
σ	the speed of the harmonic tidal constituent considered.

It is convenient also to write

$$\omega=\Omega\cos\theta, \quad \zeta'=\zeta-\bar{\zeta}.$$

We shall consider a complex harmonic constituent, so that the time enters only through the factor $e^{i\sigma t}$ and only the real parts of the functions are to be interpreted.

The equation of continuity may be written as

$$\frac{1}{a\sin\theta}\left\{\frac{\partial}{\partial\theta}(hu\sin\theta)+\frac{\partial}{\partial\chi}(hv)\right\}+i\sigma\zeta=0, \qquad (2.1)$$

and the equations of motion as

$$i\sigma u-2\omega v=-g\frac{\partial\zeta'}{a\partial\theta}-\frac{\mathrm{F}}{h}, \quad i\sigma v+2\omega u=-g\frac{\partial\zeta'}{a\sin\theta\partial\chi}-\frac{\mathrm{G}}{h} \qquad . \quad . \quad . \quad . \quad (2.2)$$

3. *The Theorem.*

We shall use a triad U, V, Z of auxiliary complex functions of θ, χ which are continuous and satisfy the differential equations

$$\frac{1}{a\sin\theta}\left\{\frac{\partial}{\partial\theta}(h\mathrm{U}\sin\theta)+\frac{\partial}{\partial\chi}(h\mathrm{V})\right\}+i\sigma\mathrm{Z}=0, \qquad (3.1)$$

$$i\sigma\mathrm{U}+2\omega\mathrm{V}=-g\frac{\partial\mathrm{Z}}{a\partial\theta},\quad i\sigma\mathrm{V}-2\omega\mathrm{U}=-g\frac{\partial\mathrm{Z}}{a\sin\theta\partial\chi}, \qquad (3.2)$$

over the ocean. It is to be noticed that in defining these functions we have changed the sign of ω from (2.2).

Now take any definite region of the ocean and let N denote the component along the outward drawn normal at any point on its boundary of the vector whose components in the directions of θ, χ increasing are U, V respectively. By the aid of Green's Theorem applied to this region, we deduce from (3.1), (2.2)

$$\begin{aligned}\int h\zeta'\mathrm{N}ds&=\iint\frac{1}{a\sin\theta}\left\{\frac{\partial}{\partial\theta}(h\zeta'\mathrm{U}\sin\theta)+\frac{\partial}{\partial\chi}(h\zeta'\mathrm{V})\right\}d\mathrm{S}\\&=-i\sigma\iint\zeta'\mathrm{Z}d\mathrm{S}+\iint h\left(\mathrm{U}\frac{\partial\zeta'}{a\partial\theta}+\mathrm{V}\frac{\partial\zeta'}{a\sin\theta\partial\chi}\right)d\mathrm{S}\\&=-i\sigma\iint\zeta'\mathrm{Z}d\mathrm{S}-\frac{1}{g}\iint h\{i\sigma(\mathrm{U}u+\mathrm{V}v)\\&\qquad-2\omega(\mathrm{U}v-\mathrm{V}u)\}d\mathrm{S}-\frac{1}{g}\iint(\mathrm{FU}+\mathrm{GV})d\mathrm{S}.\end{aligned}\quad . \;.\;.\; (3.31)$$

Here the line-integrals are taken round the boundary of the region considered, and the surface-integrals are taken over its area. Similarly using (2.1), (3.2) we obtain

$$\begin{aligned}\int h\mathrm{Z}vds=-i\sigma\iint\mathrm{Z}\zeta d\mathrm{S}-\frac{1}{g}\iint h\{i\sigma(u\mathrm{U}+v\mathrm{V})\\+2\omega(u\mathrm{V}-v\mathrm{U})\}d\mathrm{S},\end{aligned}\quad . \;.\; (3.32)$$

so that

$$\int h\zeta'\mathrm{N}ds-\int h\mathrm{Z}vds=i\sigma\iint\zeta\mathrm{Z}d\mathrm{S}-\frac{1}{g}\iint(\mathrm{FU}+\mathrm{GV})d\mathrm{S}. \quad . \;.\;.\; (3.4)$$

Equation (3.4) constitutes the theorem.

4. *Corollaries.*

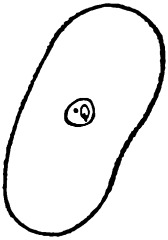
Suppose that the functions U, V, Z are specially related to a particular point Q in such a way that for any point P on a circle of centre Q

$$2\pi \,.\, \mathrm{QP} \,.\, h\mathrm{N} \to \sigma l^3 \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

as P → Q, where l is a convenient constant length. We shall say that the functions have a source at Q, at which point of course, on account of the infinity, they do not satisfy the condition of continuity laid down in § 3.

Let us suppose that U, V, Z are continuous at every point considered other than Q. Then on applying the theorem of the last section to an annular region round Q (fig. 1), we obtain, on making the inner circuit shrink into Q,

Fig. 1.



$$\sigma l^3 \zeta_{\mathrm{Q}} = \int h(\zeta' \mathrm{N} - \mathrm{Z}\nu)\,ds - i\sigma \iint \zeta \mathrm{Z}\,d\mathrm{S}, \quad . \quad . \quad (4.2)$$

on supposing that F = G = 0. In (4.2) the line-integral relates to the outer curve only and the surface-integral to the whole area which it contains.

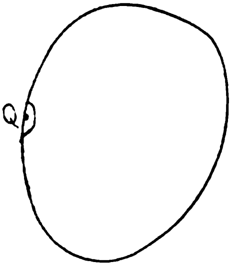
Equation (4.2) provides the means of calculating the elevation at any point inside a closed curve, providing we know the elevation and normal current all round the curve and frictional forces inside the curve may be neglected. In particular, we can calculate the elevation at any point inside a landlocked sea or ocean providing we know the coastal values. Once the functions U, V, Z have been constructed, the computations involved are of a direct and relatively simple kind.

Next suppose that Q lies on the bounding curve of the region under consideration, but that for the purpose of applying (3.4) we exclude Q by means of an arc of a circle having this point for its centre (fig. 2). We obtain, on making the circle shrink into Q,

$$\tfrac{1}{2}\sigma l^3\zeta'_Q - \int h\zeta' N\,ds = -\int hZ\nu\,ds - i\sigma\iint \bar{\zeta} Z\,dS, \quad . \quad (4.3)$$

which is an integral equation of Fredholm's type, determining ζ' on the boundary when ν is known on the boundary. This

Fig. 2.



integral equation does not appear to have been previously given, though similar equations are familiar in the theory of potential. Integral equations which have been previously proposed for the solution of tidal problems involve Green's functions.

5. *Flat Sea of Uniform Depth.*

Now let us suppose that the region under consideration is small enough for the curvature of the Earth to be neglected, and also that we may take h as constant. The equations (3.1), (3.2) may be replaced by

$$\frac{\partial^2 Z}{\partial x^2} + \frac{\partial^2 Z}{\partial y^2} + \kappa^2 Z = 0, \quad . \quad . \quad . \quad . \quad (5.1)$$

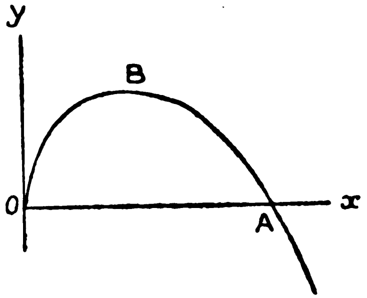
$$\left.\begin{aligned} \frac{\sigma^2 - 4\omega^2}{g\sigma} U &= i\frac{\partial Z}{\partial x} - \frac{2\omega}{\sigma}\frac{\partial Z}{\partial y}, \\ \frac{\sigma^2 - 4\omega^2}{g\sigma} V &= i\frac{\partial Z}{\partial y} + \frac{2\omega}{\sigma}\frac{\partial Z}{\partial x}, \end{aligned}\right\} \quad . \quad . \quad . \quad (5.2)$$

where $\kappa^2 = (\sigma^2 - 4\omega^2)/gh$,

and ω is now constant.

Let us first apply (3.4) to a region bounded by the coast ABO and a straight line OA (fig. 3). We shall show that when we know the tidal elevation on the coast we can calculate both the elevation and the normal current at all points along OA.

Fig. 3.



Take axes as shown and first let

$$Z = \frac{i\kappa^2 l^2}{\mu_s} \cos sx \sin \mu_s y,$$

where s is a constant, and

$$\mu_s^2 = \kappa^2 - s^2.$$

This satisfies (5.1) and on OA makes

$$Z = 0, \quad hN = -hV = \sigma l^2 \cos sx. \quad . \quad . \quad (5.31)$$

On applying (3.4) we obtain, if $OA = b$,

$$\int_0^b \zeta' \sigma l^2 \cos sx\, dx + \int_{ABO} h\zeta' N\, ds = i\sigma \iint \zeta Z\, dS. \quad (5.32)$$

Now suppose that $b = m\pi/s$ where m is any integer. Then

$$\int_0^b \zeta' \sigma l^2 \cos sx\, dx = \frac{m}{s} \sigma l^2 \int_0^\pi \zeta' \cos m\xi\, d\xi, \quad . \quad (5.33)$$

and gives the coefficient of a Fourier's cosine-series for ζ' along OA. As m is at our disposal, we thus see that we can calculate the terms of this series when we know ζ over the sea and ζ' round the coast.

Next take

$$\frac{Z}{l} = \cos sx \cos \mu_s y + \frac{2\omega s}{i\sigma\mu_s} \sin sx \sin \mu_s y, \quad . \quad (5.41)$$

which also satisfies (5.1). On OA this makes

$$Z = l \cos sx, \quad hN = -hV = 0, \quad . \quad . \quad (5.42)$$

so that on substituting into (3.4) we obtain

$$\int_{ABO} h\zeta' N\, ds - \int_0^b hv\, l \cos sx\, dx = i\sigma \iint \zeta Z\, dS. \quad (5.43)$$

Again,

$$\int_0^b h\nu l \cos sx\,dx = \frac{m}{s} lh \int_0^\pi \nu \cos m\xi\,d\xi, \quad . \quad (5.44)$$

and we see that we can evaluate the terms of the Fourier's cosine-series for ν on OA.

To illustrate the formulæ of § 4 let us take

$$Z = \tfrac{1}{4} i\kappa^2 l^3 \mathrm{K}_0(\kappa r) \quad . \quad . \quad . \quad . \quad . \quad (5.51)$$

where $\mathrm{K}_0(\ )$ denotes the Bessel's function of zero order and second kind. This makes the radial and transverse components of the vector $(h\mathrm{U}, h\mathrm{V})$ respectively equal to

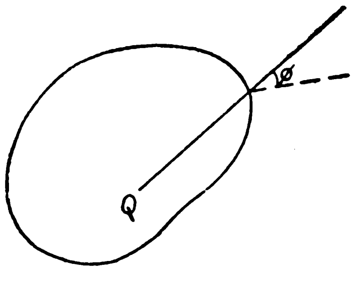
$$-\tfrac{1}{4}\sigma l^3 \frac{\partial}{\partial r} \mathrm{K}_0(\kappa r, \quad -\tfrac{1}{4}\sigma l^3 \frac{2\omega}{i\sigma}\frac{\partial}{\partial r} \mathrm{K}_0(\kappa r), \quad . \quad (5.52)$$

and therefore the value of $h\mathrm{N}$ is given by

$$-\tfrac{1}{4}\sigma l^3 \left\{ \cos\phi - \frac{2\omega}{i\sigma} \sin\phi \right\} \frac{\partial}{\partial r} \mathrm{K}_0(\kappa r), \quad . \quad (5.53)$$

where ϕ is the angle between the outward drawn normal

Fig. 4.



and the radius vector from Q (fig. 4). The expression (5 53) may equally well be written

$$-\tfrac{1}{4}\sigma l^3 \left(\frac{\partial}{\partial n} - \frac{2\omega}{i\sigma}\frac{\partial}{\partial s} \right) \mathrm{K}_0(\kappa r). \quad . \quad . \quad (5.531)$$

Equation (4.2) then takes the form

$$4\zeta_{\mathrm{Q}} = -\int \left\{ \zeta \left(\frac{\partial}{\partial n} - \frac{2\omega}{i\sigma}\frac{\partial}{\partial s} \right) - \frac{\kappa^2}{i\sigma} h\nu \right\} \mathrm{K}_0(\kappa r)\,ds + \kappa^2 \iint \zeta \mathrm{K}_0(\kappa r)\,d\mathrm{S}. \quad (5.54)$$

If we next suppose that the sea is non-rotating so that

$\omega=0$ and

$$h\nu=\frac{i\sigma}{\kappa^2}\frac{\partial\zeta'}{\partial n},$$

equation (5.54) becomes

$$4\zeta_Q=-\int\left\{\zeta'\frac{\partial}{\partial n}\mathrm{K}_0(\kappa r)-\mathrm{K}_0(\kappa r)\frac{\partial\zeta'}{\partial n}\right\}ds$$
$$+\kappa^2\iint\zeta\mathrm{K}_0(\kappa r)d\mathrm{S}. \qquad (5.541)$$

If we still further restrict by supposing that there are no disturbing forces, so that $\bar{\zeta}=0$, we obtain a result given by Lamb * except that we have taken $\mathrm{K}_0(\kappa r)$ instead of $\mathrm{D}_0\,\kappa r)$. The use of the real function $\mathrm{K}_0(\kappa r)$ instead of the complex function $\mathrm{D}_0(\kappa r)$ is legitimate when the region under consideration does not extend to infinity, as the two functions only differ by an imaginary multiple of $\mathrm{J}_0(\kappa r)$ which has no sources in any finite region. We thus see that (4.2) is a generalization of the formula given by Lamb so as to cover the extra circumstances of curvature and rotation of the Earth, variable depth and the action of disturbing forces.

The integral equation (4.3) takes the form

$$2\zeta'_Q+\int\zeta'\left(\cos\phi-\frac{2\omega}{i\sigma}\sin\phi\right)\frac{\partial}{\partial r}\mathrm{K}_0(\kappa r)ds$$
$$=\frac{\kappa^2}{i\sigma}\int h\nu\mathrm{K}_0(\kappa r)ds+\kappa^2\iint\bar{\zeta}\mathrm{K}_0(\kappa r)d\mathrm{S}. \quad . \quad . \quad (5.55)$$

Now the principal part of $\partial\mathrm{K}_0(\kappa r)/\partial r$ as $r\to 0$ is $-2/\pi r$, and we see that all the integrals are convergent, except that containing $\sin\phi$ as a factor, which is semi-convergent. From the way in which the equation was obtained it is clear that we must interpret this integral as the limit of that obtained by excluding an arc of centre Q, when the length of this arc tends to zero, *i. e.* as the "principal value" in Cauchy's sense.

6. *Ocean of Uniform Depth.*

Suppose that

$$\left.\begin{aligned}\frac{4\Omega^2a^2}{gh}\frac{\mathrm{U}}{\sigma a}&=-i\mathrm{U}_r.\sin^{r-1}\theta.e^{-is\chi}\\ \frac{4\Omega^2a^2}{gh}\frac{\mathrm{V}}{\sigma a}&=-\mathrm{V}_r.\sin^{r-1}\theta.e^{-is\chi}\\ \frac{\mathrm{Z}}{h}&=\ \mathrm{Z}_r.\sin^r\theta.e^{-is\chi}\end{aligned}\right\}, \quad . \quad . \quad (6.1)$$

---

* 'Hydrodynamics,' Art. 305.

where U_r, V_r, Z_r are functions of θ only, and r, s are numerical constants.

It is found* that both for $r=s$ and $r=-s$ solutions of (3.1), (3.2) exist which make U_r, V_r, Z_r finite at the Equator and the North Pole. We shall fix their magnitudes by supposing that $U=1$ when $\theta=0$.

When $r=s$ we shall call the solution

$$U_s^+,\ V_s^+,\ Z_s^+,$$

and when $r=-s$ we shall call the solution

$$U_{-s}^-,\ V_{-s}^-,\ Z_{-s}^-.$$

It is to be noticed that in the above s may be either positive or negative.

Let us suppose that an ocean does not extend to the North Pole, and let us consider only that part of it which lies to the north of co-latitude $\alpha(\angle\frac{1}{2}\pi)$. Let us also suppose that the parallel of co-latitude α strikes the coast at $\chi=0$ and $\chi=m\pi/s$, m being an integer which determines s.

Now consider the solution of (3.1), (3.2), in which

$$\frac{gh}{4\Omega^2a^2}\frac{Z}{h}=\tfrac{1}{2}ie^{-is\chi}\frac{\sin^s\theta Z_s^+/p_s-\sin^{-s}\theta Z_{-s}^-/q_{-s}}{P_s/p_s-Q_{-s}/q_{-s}}$$

$$+\tfrac{1}{2}ie^{is\chi}\frac{\sin^{-s}\theta Z_{-s}^+/p_{-s}-\sin^s\theta Z_s^-/q_s}{P_{-s}/p_{-s}-Q_s/q_s},\quad (6.21)$$

where

$$p_s,\ p_{-s},\ q_s,\ q_{-s}$$

denote respectively the values of

$$\sin^s\theta\,.\,Z_s^+,\ \sin^{-s}\theta\,.\,Z_{-s}^+,\ \sin^s\theta\,.\,Z_s^-,\ \sin^{-s}\theta\,.\,Z_{-s}^-$$

for $\theta=\alpha$, and

$$P_s,\ P_{-s},\ Q_s,\ Q_{-s}$$

denote respectively the values of

$$\sin^{s-1}\theta\,.\,U_s^+,\ \sin^{-s-1}\theta\,.\,U_{-s}^+,\ \sin^{s-1}\theta\,.\,U_s^-,\ \sin^{-s-1}\theta\,.\,U_{-s}^-$$

for $\theta=\alpha$. We shall then have for $\theta=\alpha$

$$Z=0,\ U=\sigma a\cos s\chi.$$

On applying (3.4) we therefore obtain

$$\int_0^{m\pi/s}h\zeta'\,.\,\sigma a\cos s\chi\,.\,a\sin\alpha d\chi+\int h\zeta' N ds=i\sigma\iint\zeta Z dS,\quad (6.22)$$

where the line-integral is taken round the coast of the ocean and the surface-integral over the surface of the ocean, in each case north of $\theta=\alpha$ only.

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* See G. R. Goldsbrough, Proc. Lond. Math. Soc. (2) xiv. pp. 31–66.

Now

$$\int_0^{m\pi/s} h\zeta'\sigma a\cos s\chi \,.\, a\sin\alpha\, d\chi=\frac{m\sigma a^2 h\sin\alpha}{s}\int_0^{\pi}\zeta'\cos m\xi\, d\xi,$$

and we thus have the coefficient of a Fourier's cosine-series for ζ' along the parallel of co-latitude α. As m is at our disposal we can thus evaluate ζ' along any parallel of latitude when we know its values round the coast, and those of ζ over the ocean.

Again, when

$$\frac{Z}{h}=\tfrac{1}{2}e^{-is\chi}\frac{\sin^s\theta Z_s^+/P_s-\sin^{-s}\theta Z_{-s}^-/Q_{-s}}{p_s/P_s-q_{-s}/Q_{-s}}$$

$$+\tfrac{1}{2}e^{is\chi}\frac{\sin^{-s}\theta Z_{-s}^+/P_{-s}-\sin^s\theta Z_s^-/Q_s}{p_{-s}/P_{-s}-q_s/Q_s}, \quad . \quad (6.31)$$

we have

$$Z=h\cos s\chi,\quad hU=0,$$

on $\theta=\alpha$, so that (3.4) will yield

$$\int h\zeta' N\, ds-\int_0^{m\pi/s} h\nu\,.\,h\cos s\chi\,.\,a\sin\alpha\, d\chi=i\sigma\iint\zeta Z\, dS, \quad (6.32)$$

the integrals being taken as in (6.22). Again, we see that we can evaluate ν through its Fourier's series along any parallel of latitude.

LXII. *On Kinematics.*

By CHARLES L. R. E. MENGES *.

THE following concerns the modern views related to electromagnetism. This subject being treated so clearly and concisely in Prof. J. H. Jeans' well-known excellent book †, a quotation therefrom will be the best beginning to attach my explanations.

Page 607 reads:—"In Fizeau's water-tube experiment, a stream of water was made to flow through a tube, its velocity of flow being u relative to the earth, and a ray of light was passed through the water in the direction of its motion. To an observer moving with the stream, the water would appear to be at rest, so that the light would be propagated relatively to this observer with a velocity u' connected with the refractive-index ν of the water by the relation (C = velocity of light in vacuo)

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* Communicated by the Author.

† J. H. Jeans, 'The Mathematical Theory of Electricity and Magnetism' 4th edition (Cambridge, at the University Press, 1923).

$$u' = \frac{C}{\nu}. \quad \ldots \ldots \ldots \quad (1)$$

"According to classical laws of kinematics, the light ought to travel, relative to an observer at rest on the earth, with a velocity

$$u' + u \quad \ldots \ldots \ldots \quad (2)$$

or

$$\frac{C}{\nu} + u. \quad \ldots \ldots \ldots \quad (3)$$

"Fizeau found it possible to measure the actual velocity by an interference method and formula (3) was not confirmed. The formula

$$\frac{C}{\nu} + u\left(1 - \frac{1}{\nu^2}\right) \quad \ldots \ldots \quad (4)$$

was found to represent the velocity accurately both for water and other transparent media."

The generally admitted inference is:—

By applying the laws of kinematics to Fizeau's water-tube experiment, formula (3) is obtained, and this formula was not confirmed by experiments. Therefore those laws of kinematics are not true.

This conclusion is derived from results obtained by means of a moving *liquid*, water, which has obvious practical advantages for the experiment. But the theory, the kinematical insight of the question, is more intricate when the light-waves propagate in a *motionless* tube, wherein water flows, than when they traverse a moving *solid* transparent substance. It is therefore of importance, that formula (4) for flowing water has been very accurately confirmed indirectly by Prof. P. Zeeman's experiments on Fizeau's effect in moving *solid* transparent substances *.

The following concerns in particular Fizeau's effect in moving transparent *solids*.

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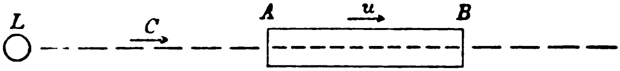
* P. Zeeman, *Verslagen Akadem. Amsterdam*, xxvii. p. 1453 (1919).

In Zeeman's experiment the source of light L sends a ray through a glass cylinder AB moving with the velocity u relative to L. When the glass cylinder is still at rest, the frequency n^0 of the light-waves in it is the same as in the



source L. Then the light-waves propagate with velocity u^0 in the glass, its refractive index being ν^0 according to the relation

$$u^0 = \frac{C}{\nu^0}. \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

We know that the refractive index of glass, when at rest, varies with the frequency of the light-waves. The frequency in the glass being n instead of n^0, the refractive index is by Lorentz's formula * :

$$\nu = \nu^0 + (n - n^0)\frac{d\nu^0}{dn^0}. \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

When the frequency of the source L remains n^0, but the glass is moving with velocity u in the direction of the propagating light-waves, then the frequency in the glass is no longer n^0. By Doppler's effect it is then

$$n = n^0 \frac{C - u}{C}. \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

Lorentz improved Fresnel's original formula with ν^0, by replacing ν^0 by ν from equation (6). The velocity u may be introduced in equation (6) by replacing $n - n^0$ by its value from equation (7). But it must be well understood that $\frac{d\nu^0}{dn^0}$ in equation (6) is not in the least related with movement; its value is taken from experiments *without any material movement*. Therefore, with ν according to equation (6) instead of ν^0, only a difference in frequency *apart from motion* is taken into account, but not that part of the observed total effect, which in particular results from motion.

To discuss the question clearly, three exactly defined cases will be considered.

Case 1: The source of light L with frequency n^0 and the glass cylinder *at rest*; the frequency in the glass is also n^0.

Case 2: *Without material movement* as in case 1, but the frequency of the source L and in the glass AB both being now n instead of n^0.

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* H. A. Lorentz, 'The Theory of Electrons,' p. 191; and note 69, p. 316 (B. G. Teubner, Leipzig, 1909).

CASE 3: *As in case* 2 the frequency of the light-waves is n *in the glass* AB, which, however, is now *moving* away from L with velocity u.

In this last case with the *moving* glass cylinder (Zeeman's experiment), the frequency in the source of light L must differ from n because of Doppler's effect. But immediate action at a distance is excluded, therefore the different frequency in L cannot *by itself* produce in the *distant* glass cylinder AB an effect differing from that in case 2. As experiment proves beyond any doubt that the optical effect in case 3 is really different from that in case 2, there must exist in the field, immediately in contact with the glass face A, in case 3 something which differs from that in case 2. Now, in case 2 *without material motion*, the velocity of the light-waves which fall on the face A is C. But in case 3 the face A *is moving* with velocity u relative to its position in case 2, where it receives the waves with velocity C. Therefore in case 3 the speed wherewith the *moving face* A *receives* the waves is *by kinematics* equal to $C-u$.

This being taken into account, I showed * by pure mathematics and kinematics, without introducing a "dragging coefficient" or any hypothesis of that kind, that ν in formula (1)—to make it kinematically correct for a moving substance be it water or glass—must be replaced by

$$\nu' = \nu - \frac{u}{C}(\nu^0 - 1). \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The true formula for u' in moving glass is then

$$u' = \frac{C-u}{\nu'} = \frac{C-u}{\nu - \frac{u}{C}(\nu^0-1)} \quad . \quad . \quad . \quad . \quad (1a)$$

It is now easy to explain the above given quotation: "Fizeau found it possible to measure the actual velocity and formula (3) was not confirmed."

For formula (3), namely

$$\frac{C}{\nu} + u, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is obtained by inserting in formula

$$u' + u \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the value of u' from

$$u' = \frac{C}{\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

---

* *Comptes Rendus*, clxxv. p. 574 (1922).

Formula (2) being taken in accordance with perfectly true laws of kinematics, then it will certainly become false, if the true value of u' be replaced by a value which is contradictory with said laws. This is the case with formula (3), because of the false value of u' from equation (1), which ought to be true for the *moving* glass. But in this sense C in it is certainly inconsistent with the laws of kinematics, as I above explained ; C must be replaced by $C-u$, giving the kinematically correct formula (1*a*).

Instead of the hitherto generally admitted inference that the laws of kinematics, as expressed in formula (2), are not correct, the true inference now is quite inverse. *For according to the laws of kinematics formula* (1) *must be replaced by formula* (1*a*), *and this is exactly confirmed by Zeeman's very accurate experiments.* It follows from the formula confirmed by Zeeman's experiments, his formula being obtainable from my new formulæ (1*a*) and (8) by pure mathematical transformations, as follows.

The glass cylinder of length l being at rest, the speed of the light-waves therein is $u^0=\frac{C}{\nu^0}$, and it contains

$$l:\frac{u^0}{n^0}=\frac{ln^0}{u^0}$$

waves. While the glass cylinder moves it contains

$$\frac{ln}{u'}$$

waves. The optical effect of motion is therefore

$$l\left(\frac{n^0}{u^0}-\frac{n}{u'}\right),$$

and with u' from formula (1*a*) it is

$$l\left(\frac{n^0}{\frac{C}{\nu^0}}-\frac{n^0\frac{C-u}{C}}{\frac{C-u}{\nu'}}\right)=\frac{ln^0}{C}(\nu^0-\nu')\,.$$

With formulæ (6), (7), (8) and the wave-length $\lambda=\frac{C}{n^0}$ this optical effect is

$$\frac{lu}{C}\left(\nu^0-1-\lambda\frac{d\nu^0}{d\lambda}\right),$$

which is Zeeman's formula.

LXIII. *The Proof of the Corollary of Carnot's Theorem.*

By ARTHUR E. RUARK[*].

THERE are many methods for proving by the use of the first and second laws of thermodynamics the theorem that "All reversible engines working between the same temperatures have equal efficiencies."

So far as I can find, it has not been pointed out that this statement may be derived by using the first law together with a postulate which *denies* the validity of the second law. This postulate may be stated in the form: It is impossible for any self-acting mechanism working in a complete cycle to produce work continuously by transferring heat from a higher to a lower level of temperature without producing any other effect.

Let us first consider the usual proof of this theorem. Let there be two reversible engines, 1 and 2, such that in a single cycle each does work W. Engine 1 takes in heat Q_1 from the hot bath and gives heat q_1 to the cold bath, while engine 2 takes in Q_2 and rejects q_2. We have

$$Q_1 - q_1 = W = Q_2 - q_2,$$

whence

$$Q_1 - Q_2 = q_1 - q_2.$$

If engine 1 drives engine 2 in a reverse direction, the hot bath loses $Q_1 - Q_2$ and the cold bath gains $q_1 - q_2$. By the second law

$$Q_1 - Q_2 \geqq 0.$$

But if engine 2 drives engine 1 reversely, we find in exactly similar manner that

$$Q_2 - Q_1 \geqq 0.$$

Therefore $Q_1 = Q_2$, $q_1 = q_2$, and

$$\frac{W}{Q_1} = \frac{W}{Q_2}.$$

If we say, on the contrary, that the hot bath gains heat at the expense of the cold bath, we have in the first experiment

$$Q_1 - Q_2 \leqq 0,$$

and in the second

$$Q_2 - Q_1 \leqq 0,$$

leading to the same conclusion as before.

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[*] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

The interest lies in the fact that deductions from the theorem "All reversible engines working between the same temperatures have equal efficiencies" cannot be used as the basis of experiments designed to test the validity of the second law. It will be understood, of course, that the above objections do not apply to the theorem "A non-reversible engine cannot be as efficient as a reversible engine working between the same temperatures." It is only the preceding statement concerning all reversible engines which can be proved by postulating the opposite of the second law.

Bureau of Standards,
October 30, 1924.

LXIV. *The Influence of Temperature on the Intensity of Reflexion of X-Rays from Rocksalt.* *By* R. W. JAMES, *M.A., Senior Lecturer in Physics in the University of Manchester* [*].

CONTENTS.

1. Introductory.
2. Previous experimental work.
3. Description of experiments.
4. Permanent effects of heat on the reflecting power of rocksalt.
5. Results of observation.
6. Correction of observations.
7. Discussion of results and deduction of an empirical law to fit them.
8. Comparison with Debye's theory.

1. A THEORETICAL expression for the influence of temperature on the intensity of the interference maxima produced when X-rays are diffracted by a crystal was first obtained by Debye [†] in 1913. Suppose a beam of X-rays of wave-length λ passes through a crystal in a direction making a glancing-angle θ with a series of atomic planes whose spacing is d. Then the spectrum of the nth order may be considered as produced by reflexion at these planes, if

$$2d \sin\theta = n\lambda.$$

If the atoms lie exactly in the plane, the contributions from all of them to this spectrum will be exactly in phase; but if, by reason of their heat-motion, they are displaced by varying small amounts from these planes, the contributions will no longer all be in phase, and the intensity of the spectrum will be correspondingly reduced. Debye in his earliest papers supposed each atom to be bound by a quasi-elastic force to a position of equilibrium lying in the atomic plane, or rather at one of the lattice points of the crystal. Owing to the heat motion, each atom is displaced at any instant by a certain distance from its equilibrium position. If we knew all the displacements at any time, we could calculate the effect on the intensity of the X-ray beam diffracted in any direction. Debye carried out the calculation for a given configuration, multiplying the intensity factor so obtained by the probability of the occurrence of the configuration, and summing up over all possible configurations obtained a value for the mean intensity of the diffracted beam in any direction. The probability of a given set of displacements was calculated according to Maxwell's distribution law. Debye obtained an expression for the intensity of the X-ray beam in any direction which consisted of two parts—the first corresponding to the scattered radiation, the second to the interference maxima. The effect of increasing temperature is to increase the scattered radiation and to diminish the intensity of the interference maxima. Debye's early calculation showed that to account for the effect of the temperature movement, the intensity of the scattered radiation had to be multiplied by a factor

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[*] Communicated by Prof. W. L. Bragg, M.A., F.R.S.

[†] P. Debye, *Verh. der deutsch. Phys. Ges.* xv. pp. 678, 738, and 867 (1913).

$$\left(1-e^{-\frac{16\pi^2 kT}{f\lambda^2}\sin^2\frac{\phi}{2}}\right),$$

while that of the interference maxima had to be multiplied by a factor

$$e^{-\frac{16\pi^2 kT}{f\lambda^2}\sin^2\frac{\phi}{2}},$$

where T is the absolute temperature, k the gas constant, f the quasi-elastic force per unit displacement of the atom, and ϕ the angle which the diffracted beam makes with the incident beam, so that if the spectrum is supposed to be formed by reflexion from a set of planes at a glancing angle θ, $\theta=\phi/2$.

The use of the Maxwell-Boltzmann distribution law in the above calculation is equivalent to assuming that the displacements of the atoms are all independent. It is evident, however, that this assumption is not justified. The atoms are not held to fixed points of equilibrium, but to one another, and the displacements of any atom must influence those of its neighbours. The heat-motion of such a medium may be considered as a series of "elastic waves," and had been discussed by Born and Karman[*]. Debye[†] recalculated the effect of heat-motion on the interference maxima, using these ideas and taking the quantum theory into account. He found that the intensity of the interference maxima had to be multiplied by a factor e^{-M}, where

$$M = \frac{6h^2}{\mu k\lambda^2\Theta} \cdot \sin^2\frac{\phi}{2} \cdot \frac{\phi(x)}{x} \quad . \quad . \quad . \quad . \quad (1)$$

Here μ is the mass of one of the atoms, h is Planck's constant, Θ a temperature characteristic of the crystal, $x=\frac{\Theta}{T}$, and $\phi(x)$ is a certain function of $\frac{\Theta}{T}$ which can be evaluated. If the existence of Nullpunktsenergie is assumed, $\frac{\phi(x)}{x}$ is replaced by $\left\{\frac{1}{4}+\frac{\phi(x)}{x}\right\}$. For values of T small compared with the characteristic temperature Θ, M should be proportional to T^2, while for high values of T it should be proportional to T, as the more elementary treatment showed.

More recently the question of the effect of temperature on the scattered radiation has been considered by Faxen[‡] and by Waller[§].

2. The first experiments on the influence of temperature on the intensity of reflexion of X-rays by crystals were carried out in 1914 by Sir William Bragg[||], who used rocksalt and sylvine. With rocksalt, experiments were made at temperatures of 15° and 370° C., and the conclusion was reached that the effect was of the same order as that calculated by Debye. More recently experiments on similar lines have been made by Backhurst[¶], who used aluminium, corundum, carborundum, diamond, and graphite. Only very general agreement was found with the theory of Debye, but it must be noticed that Debye's theory applies to a simple cubic lattice only. Quite recently Collins[**] has studied the Debye effect for aluminium, and again finds results at variance with the theory of Debye. The

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[*] Born and Karman, *Phys. Zeitschr.* xiv. p. 65 (1913).

[†] *Ann. der Phys.* xliii. p. 49 (1914).

[‡] H. Faxen, *Zeitsch. für Physik.* xvii. p. 266 (1923).

[§] L. Waller, *ibid.* p. 398 (1923).

[||] W. H. Bragg, Phil. Mag. May 1914.

[¶] Proc. Roy. Soc. A, cii. p. 340 (1922).

[**] E. H. Collins, Phys. Rev. xxiv. p. 152 (1924).

effect of temperature on the scattered radiation has been studied experimentally by G. E. M. Jauncey [*].

3. The experiments to be described in the present paper had their origin in some work by Professor W. L. Bragg [†], C. H. Bosanquet, and the writer on the intensity of reflexion of X-rays from rocksalt, in which an attempt was made to get some idea of the distribution of the electrons in the atoms of sodium and chlorine. In the course of this work it was necessary to make allowance for the Debye factor. The only figures available for rocksalt were those of Sir W. H. Bragg obtained in 1914, and it was considered desirable to repeat them with the better apparatus at our disposal, and if possible to extend the temperature range in both directions. The intensities of reflexion were measured by the method first used by W. H. Bragg [‡], and described in detail by W. L. Bragg, James, and Bosanquet in the papers quoted. The crystal was mounted on the table of an ionization spectrometer. The ionization chamber was set at the angle appropriate to the spectrum under investigation, with a slit wide enough to receive the whole reflected beam, including both the α and α' peaks, and the crystal was rotated at a uniform angular velocity through the range of angles over which it reflected. The total quantity of electricity passing across the ionization chamber during the sweep of the crystal was measured. Let this be proportional to E. Then if ω is the angular velocity with which the crystal is swept, and I the quantity of electricity passing in unit time when the beam is allowed to enter the chamber directly, the quantity $\frac{E\omega}{I}$ is a constant for a given crystal face, and can be taken as a measure of the reflecting power of that face. The quantity $\frac{E\omega}{I}$ is called by Darwin the "integrated reflexion"—a convenient term which will be employed here.

The source of radiation was a Coolidge bulb with either a rhodium or a molybdenum anticathode. To supply the current, a transformer operated by a rotary converter of about 2·25 kilowatts capacity worked from the Corporation mains and producing alternating current at about 140 volts was used. The potential employed was usually about

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[*] Jauncey, Phys. Rev. xx. p. 421 (1922).

[†] Phil. Mag. xli. p. 309 (1921); xlii. p. 1 (1921); xliv. p. 433 (1922).

[‡] *Loc. cit.*

50,000 volts. With this arrangement it was found possible to keep the intensity of the X-ray beam far steadier than in the earlier experiments*, when a coil and mercury break were used. A null method was used in the observations. The string of the electrometer, which was of the Lutz-Edelmann type, was connected to the inner plate of a condenser, whose outer coating could be raised to any desired potential by means of a potential divider. The sign of the potential applied to the outer coating was such as to neutralize by induction the charge received by the electrometer due to the ionization current. The potential necessary to bring the string back to its zero is then proportional to the total charge received by the electrometer during the observation. The actual readings taken were thus the readings on the potential divider, which had one hundred divisions. A maximum potential of 6 volts could be applied, and to increase the range of reading, any desired fraction of the potential could be tapped off by means of a post-office box and applied to the potential divider. The range of the instrument could be increased still further by having several inner plates of different sizes for the condenser. In this way spectra differing greatly in their absolute intensity could be compared.

The crystal was held between two jaws lined inside with asbestos, on an iron stand to which the necessary adjustments for tilt and centring could be given. The stand was mounted on an asbestos sheet supported on brass and insulated from the spectrometer table by a fused silica ring 3 cm. in height packed with kieselguhr. Over the crystal fitted a cylindrical electric furnace wound with "nichrome" wire and provided with mica windows to allow the ingress and egress of the X-rays. The furnace was surrounded by a cylinder of sheet asbestos pierced with suitable openings, and radiation downwards to the spectrometer table was further checked by surrounding the silica tube, on which the furnace was mounted, by a broad collar of asbestos sheeting. The arrangement for heat insulation proved very satisfactory, and it was possible to work for hours with the crystal at red heat with the spectrometer table only slightly warm. The whole furnace, including the silica pedestal, could be lifted off the spectrometer table and replaced while hot, so that alternate readings with the heated crystal and with the standard could be made. It was found that no appreciable change in temperature was produced by removing the furnace from the spectrometer and placing it on another stand close beside it.

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* Bragg, James, and Bosanquet, *loc. cit.*

The temperature was measured by a thermocouple of iron-constantan placed in contact with the crystal face in such a position that the X-rays did not strike it. The e.m.f. generated by the couple was measured directly with a very convenient potentiometer, kindly lent for these experiments by the Cambridge and Paul Scientific Instrument Company, to whom my best thanks are due. The thermocouple and potentiometer were calibrated, using the boiling-point of water and the melting-points of tin, lead, zinc, antimony and aluminium, and from the readings so obtained a temperature-e.m.f. curve was drawn. Very closely similar curves were obtained with the different couples used, and the error in temperature should not be more than a few degrees. To ensure steadiness and uniformity of temperature, the crystal was heated for from one to two hours before readings were taken.

To determine the proper setting of the ionization chamber, which varies with the temperature on account of the expansion of the crystal and the consequent alteration in the spacing *d*, a series of readings were made in the region of the peak, the setting of the chamber being altered half a degree at a time, with a corresponding change in the crystal sweep. To determine the intensity of the peak, readings were taken with the chamber two degrees above and two degrees below the setting of the peak, where only the general continuous radiation from the bulb could enter it. The mean of these readings was subtracted from that corresponding to the peak, and the difference was taken as the intensity of the peak. The allowance for the general radiation is of considerable importance, since at high temperatures it may in some cases account for as much as 70 per cent. of the radiation entering the chamber at the setting of the peak. It should be noticed that any creep of the electroscope due to natural leak, or to scattered radiation, is included in the allowance for general. These factors remain practically constant as the intensity of the peak diminishes, and the increasing fraction of general radiation is no doubt largely due to this fact, although, in the case of high-order spectra, the general radiation will include reflexions of longer wave-length at lower orders, for which the decrease of intensity with temperature will be less than for the peak, and this also will cause an increase in the percentage of general as the temperature rises.

The intensity of reflexion from the crystal under investigation was compared in each case with the reflexion from the same face and the same order from a standard rocksalt crystal.

A typical comparison began with a determination of the percentage of general radiation for the heated crystal Q, and ended with a similar determination for the standard S. After the determination for Q, a series of alternate sets of readings at the peak-settings of Q and S were taken in rapid succession, Q being removed from the spectrometer and replaced by S, and so on. The mean values for Q and S obtained from these alternate readings are corrected by subtracting from each the appropriate percentage of general, and the ratio of the corrected values is taken as the ratio of the intensities of the two spectra.

4. Some difficulty was experienced in finding a crystal of rocksalt suitable for these experiments. It was found that all crystals which had a turbid appearance were destroyed on heating, owing to the swelling and bursting of the small liquid or gaseous inclusions which they contained. If care was taken to choose a perfectly clear crystal containing no inclusions, this difficulty could be overcome completely. Even with such crystals it was found that the intensity of reflexion became smaller after continued heating. A similar effect was noticed by Backhurst[*], who ascribed it to the breaking down of one complete crystal into smaller ones differently oriented. It does not seem certain, however, that this is the true explanation, at any rate in the case of rocksalt; indeed, there is some reason to believe that the reverse may be true, and that the size of the homogeneous crystal elements may be increased by heating. The effect in question is much more marked with the first-order reflexion from the (100) face than with the second, and with the second it is more marked than with the third; and this appears to be the case whether the reflexion takes place from a face, or through a slip of crystal in the manner employed in determining the absorption coefficient at the reflecting angle[†]. For example, in some preliminary experiments with a slip of crystal about 1 mm. thick, the intensity (100) before heating was found to be 0·71 of the standard. After heating to 590° C., the intensity had fallen to 0·50 of the standard, but after the

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[*] Backhurst, Proc. Roy. Soc. A, cii. p. 340 (1922).

[†] Bragg, James, and Bosanquet, Phil. Mag. July 1921, p. 1.

crystal had cooled, the intensity had only risen to 0·53. The intensity (200) before heating was 0·92; on heating to 590° it fell to 0·43 and rose on cooling to 0·83, and the permanent fall for (300) was still smaller. This behaviour suggests strongly that the effect of heating is to increase the special absorption or "extinction coefficient" of the crystal. This would have a far greater influence on the intensity of the strong (100) than on the weaker (200) and (300), and might be accounted for by a more perfect crystallization of the material of the slip. The effect is not confined entirely to the surface layers, since reflexion at a slip occurs throughout the whole thickness. The phenomenon requires investigation in much greater detail, and this work is being undertaken. Experiments showed that for (200) and spectra of higher orders, a steady state appears to be reached after several heatings to 500° or 600°. The values of the intensities are less by a few per cent. than those before heating, but are permanent in the sense that the intensities before heating and after heating, when the crystal has been allowed to cool again, are the same. No consistent values for (100) could be obtained, and consequently this spectrum was not used in the present set of experiments.

5. All the observations to be described were made by reflexion at a face. The first set of observations were made with the (300) spectrum, rhodium radiation being used. The rhodium anticathode contained ruthenium as an impurity, and the ruthenium lines caused a certain amount of trouble in determining the general radiation; so, later, the rhodium bulb was replaced by one having a molybdenum target, and with this a series of observations were made between 15° and 650° C., using the (200), (300), and (400) spectra. The results of the measurements are given in Table I.

In this table, column (1) gives the absolute temperature; column (2), R the intensity actually observed, expressed in terms of the reflexion from the corresponding face of the standard crystal at 19° C. as unity. Column (3) gives the ratio of R_T, the observed intensity, corrected in the manner described below, to R_1 the mean corrected intensity at room temperature.

TABLE I.

Rh Kα radiation. $\lambda = 0{\cdot}615$ Å.

	(1) T.	(2) R.	(3) $\frac{R_T}{R_1}$.	(4) $T^2\left(\frac{\sin\theta}{\sin\theta_1}\right)^2$.	(5) $\log_{10}\frac{R_T}{R_1}$.	(6) $\left(\frac{\lambda}{\sin\theta_1}\right)^2\log_{10}\frac{R_T}{R_1}$.
(300) $\theta_1 = 19°\ 10'$ $\sin\theta_1 = 0{\cdot}3283$	293	0·926	1·015	8·58 × 10⁴	+0·0064	+0·022
	292	0·911	0·998	8·53 ,,	−0·0007	−0·002
	291	0·908	0·995	8·47 ,,	−0·0020	−0·007
	292	0·906	0·991	8·53 ,,	−0·0031	−0·011
	413	0·701	0·765	16·89 ,,	−0·1163	−0·438
	472	0·621	0·677	21·95 ,,	−0·1696	−0·597
	513	0·535	0·582	25·83 ,,	−0·2347	−0·826
	615	0·357	0·388	36·83 ,,	−0·4114	−1·447
	630	0·351	0·381	38·58 ,,	−0·4190	−1·474
	670	0·304	0·330	43·51 ,,	−0·4818	−1·695
	778	0·169	0·183	58·21 ,,	−0·7379	−2·596
	862	0·115	0·124	70·98 ,,	−0·9060	−3·188
Mo Kα radiation. $\lambda = 0{\cdot}710$ Å.						
(200) $\theta_1 = 14°\ 37'$ $\sin\theta_1 = 0{\cdot}2524$	292	0·831	0·987	8·53 × 10⁴	−0·0057	−0·045
	292	0·845	1·003	8·53 ,,	+0·0016	+0·013
	292	0·850	1·009	8·53 ,,	+0·0041	+0·032
	426	0·710	0·833	18·04 ,,	−0·0793	−0·628
	579	0·595	0·692	32·69 ,,	−0·1598	−1·265
	703	0·500	0·577	46·81 ,,	−0·2390	−1·892
	843	0·362	0·413	67·94 ,,	−0·3841	−3·040
	913	0·312	0·355	79·20 ,,	−0·4500	−3·562
(300) $\theta_1 = 22°\ 15'$ $\sin\theta_1 = 0{\cdot}3786$	291	0·917	1·000	8·47 × 10⁴	0·000	0·000
	393	0·722	0·785	15·47 ,,	−0·1051	−0·370
	511	0·510	0·552	25·65 ,,	−0·2582	−0·908
	625	0·339	0·366	38·04 ,,	−0·4361	−1·535
	756	0·191	0·205	55·04 ,,	−0·6882	−2·422
	898	0·102	0·109	76·70 ,,	−0·9624	−3·387
(400) $\theta_1 = 30°\ 18'$ $\sin\theta_1 = 0{\cdot}5045$	292	0·943	0·989	8·53 × 10⁴	−0·0046	−0·009
	290	0·964	1·012	8·41 ,,	+0·0050	+0·010
	382	0·682	0·714	14·47 ,,	−0·1466	−0·290
	437	0·504	0·527	18·87 ,,	−0·2784	−0·551
	503	0·362	0·378	24·86 ,,	−0·4228	−0·837
	593	0·219	0·228	34·30 ,,	−0·6426	−1·272
	697	0·110	0·114	46·97 ,,	−0·9436	−1·867

6. The measured intensity R is proportional to the integrated reflexion $\frac{E\omega}{I}$, where E is the total energy reflected when the crystal is rotated with angular velocity ω, and I is the energy received by the ionization chamber when the incident beam enters it for one second. Now it can be shown that [*][†]

$$\frac{E\omega}{I}=\frac{N^2\lambda^3}{2\mu\sin 2\theta}\cdot\frac{e^4}{m^2c^4}\cdot F^2.\frac{1+\cos^2 2\theta}{2}\cdot e^{-bf(T)\frac{\sin^2\theta}{\lambda^2}}. \qquad (2)$$

In this formula N is the number of molecules per unit volume of the crystal, μ the linear absorption coefficient of the crystal, θ the glancing angle of reflexion, and λ the wave-length of the X-rays. e and m are the charge and the mass of an electron, and c is the velocity of light. The factor $\frac{1+\cos^2 2\theta}{2}$ allows for the fact that the incident rays are unpolarized, and the factor F^2 for the finite size of the atom—which, since the electrons producing the scattering of the X-rays are distributed throughout a region whose dimensions are comparable with the spacings of the atomic planes, adds to the spectra a contribution which depends on the angle of diffraction, becomes smaller as that angle increases, and is proportional to the number of electrons in the atom for very small angles of scattering [‡]. As the formula is written, the factor F^2 also includes the "structure factor" which depends on the arrangement of the atom in each repeat of the crystal pattern.

The term $e^{-bf(T)\frac{\sin^2\theta}{\lambda^2}}$ is the Debye factor which is under investigation in this paper.

We may write

$$e^{-bf(T)\frac{\sin^2\theta}{\lambda^2}}=\frac{E\omega}{I}\cdot\frac{4m^2c^4}{e^4\lambda^3}\cdot\frac{\mu}{N^2}\cdot\frac{\sin 2\theta}{1+\cos^2 2\theta}\cdot\frac{1}{F^2}\propto R_T. \quad . \qquad (3)$$

The measured intensity R, column (2), Table II., is proportional to $\frac{E\omega}{I}$. We require R_T, the corrected intensity, column (3), which is proportional to the value of the Debye factor at different temperatures. To obtain this it is necessary to allow for the fact that μ, N, θ, and F all depend on the temperature; μ and N are proportional to the density of the crystal, which decreases as the temperature rises owing to the thermal expansion, and for the same reason θ, the glancing angle for a given spectrum, decreases as T increases. The factor F^2 depends on $\frac{\sin\theta}{\lambda}$, and thus on the temperature. The change of θ with temperature was determined by direct measurement, and from this the value for α the coefficient of expansion of the crystal was calculated. To a sufficient approximation for the purpose under consideration, the coefficient of expansion was found to be linear over the range from 0° to 500°. The value of α obtained as a mean of several experiments was 0·0000383, which is in fair agreement with that obtained by Fizeau, 0·0000402, over a much smaller range from interference measurements. From this figure, the ratios of the values of the factors $\frac{\mu}{N^2}$ and $\frac{\sin 2\theta}{1+\cos^2 2\theta}$ at any temperature to those at room temperature were calculated directly.

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[*] C. G. Darwin, Phil. Mag. xxvii. pp. 315 and 675 (1914).

[†] A. H. Compton, Phys. Rev. ix. p. 1 (Jan. 1917).

[‡] W. L. Bragg, James, and Bosanquet, Phil. Mag. xli. p. 309 (1921); xlii. p. 1 (1921); xliv. p. 433 (1922).

The allowance for the change in F^2 presents more difficulties. The values of F^2 determined by W. L. Bragg, James, and Bosanquet * for rhodium rays were used. In order to apply these determinations to the observations made with molybdenum radiation, use was made of the fact that F is a function of $\frac{\sin\theta}{\lambda}$. If the values of F^2 obtained for rhodium radiation are plotted against $\frac{\sin\theta}{\lambda_{\mathrm{Rh}}}$, the curve obtained should be independent of the wavelength, and the value of F^2 for any angle θ for molybdenum can be read off at once over the corresponding value of $\frac{\sin\theta}{\lambda_{\mathrm{Mo}}}$. The uncertainty in this correction lies in the uncertainty of the actual values of F^2, which change rapidly with θ. The corrections for $\frac{\mu}{N^2}$ and for $\frac{1}{F^2}$ go in opposite directions, so that the total correction is not large and was not over 2 per cent. in any case, which is really within the errors of experiment.

There is one other correction to be taken into account—that for the change in the "extinction coefficient." For intense spectra the value of the linear absorption coefficient

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* Phil. Mag. xlii. p. 1 (1921).

depends on the intensity of the spectrum *; hence, as the intensity diminishes with rising temperature, the effective value of μ decreases. It has been shown that, to a fair degree of approximation,

$$\mu = \mu_0 + \epsilon = \mu_0 + k\text{R}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where μ is the effective absorption coefficient at the reflecting angle, μ_0 is the ordinary absorption coefficient of the crystal, and ϵ is the extinction coefficient, which is porportional to the observed intensity of reflexion. The values of ϵ for different spectra for rhodium radiation were determined in the paper quoted. More recently, Wasastjerna † has carried out a determination by a different method for molybdenum radiation, and this has been employed in the present paper. Wasastjerna finds that $\mu_0 = 16{\cdot}2$ and $\epsilon = 4{\cdot}4$ for (100). Assuming as a sufficient approximation that $\text{R}_{100} : \text{R}_{200} : \text{R}_{300} = 100 : 20 : 5$, we can, using (4), obtain a curve giving the value of ϵ for different values of R, and so apply the necessary correction.

The extinction correction is inappreciable for the 3rd- and 4th-order spectra, and has only been applied in the case of (200). The allowance for extinction made above is very uncertain. It is known that the extinction coefficient depends considerably on the particular crystal used, and, as we have seen, it is possible that the extinction coefficient for a rocksalt crystal which has been heated is abnormally large. All that can really be claimed is that the results corrected in the manner described are probably closer to the truth than they would have been had no correction been applied at all. In any case, the correction for the (200) spectrum is not very large.

7. The values of the corrected reflexion $\frac{\text{R}_\text{T}}{\text{R}_1}$, plotted against the absolute temperature, are shown in fig. 1.

The theory of Debye leads to the conclusion that if R_T is the corrected reflexion at temperature T; R_1 that at any standard temperature T_1 (here the room temperature); and R_0 the value of the reflexion at absolute zero, then

$$\left.\begin{aligned} \text{R}_\text{T} &= \text{R}_0 \exp\left\{-bf(\text{T})\frac{\sin^2\theta}{\lambda^2}\right\}, \\ \text{R}_1 &= \text{R}_0 \exp\left\{-bf(\text{T}_1)\frac{\sin^2\theta_1}{\lambda^2}\right\}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (5)$$

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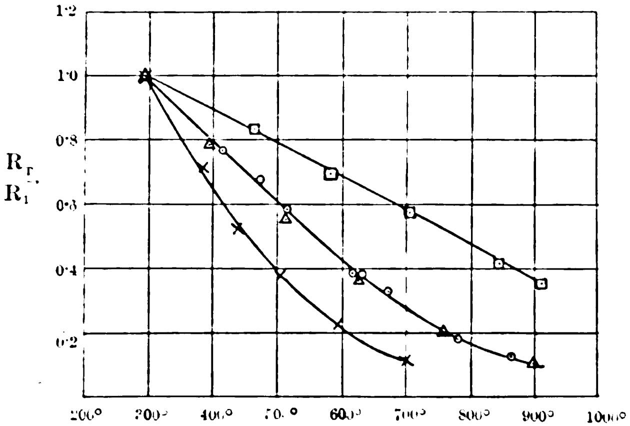
* Bragg, James, and Bosanquet, Phil. Mag. xlii. p. 1 (1921). C. G. Darwin, Phil. Mag. xliii. p. 800 (1922).

† W. A. Wasastjerna, *Soc. Sci. Fenn.* ii. p. 15.

where b is a constant, $f(\mathrm{T})$ some function of the absolute temperature, and θ and θ_1 the glancing angles at T and T_1 respectively.

Fig. 1.



Temperature of crystal in degrees absolute.

⊙ (300) Rhodium radiation. Δ (300) Molybdenum radiation.

⊡ (200) Molybdenum radiation. × (400) ” ”

Hence

$$\frac{R_T}{R_1} = \exp\left\{-\frac{b}{\lambda^2}\left(f(\mathrm{T})\sin^2\theta - f(\mathrm{T}_1)\sin^2\theta_1\right)\right\}$$

$$= \exp\left[-\frac{b\sin^2\theta_1}{\lambda^2}\left\{f(\mathrm{T})\left(\frac{\sin\theta}{\sin\theta_1}\right)^2 - f(\mathrm{T}_1)\right\}\right]; \quad . \quad . \quad . \quad (6)$$

$$= \text{const.} \times \exp\left\{-\frac{bn^2}{4d_1^2}\cdot f(\mathrm{T})\left(\frac{\sin\theta}{\sin\theta_1}\right)^2\right\}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where n is the order of the spectrum and d_1 the spacing of the atomic planes at the standard temperature T_1. Thus the curve showing the relationship between $\frac{R_T}{R_1}$ and T should be independent of the wave-length for a given order, apart from the effect introduced by the small change in the value of $\left(\frac{\sin\theta}{\sin\theta_1}\right)^2$ as the temperature changes.

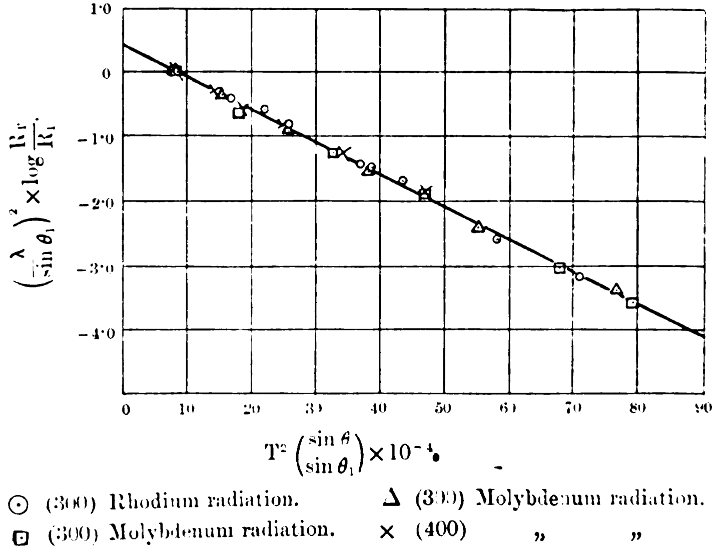
This portion of the theory is confirmed by the experiments. The curve in fig. 1 for the (300) spectrum was obtained with both rhodium and molybdenum radiation. The circles indicate the points obtained with rhodium radiation, the triangles those with molybdenum, and it will be seen that both sets of points lie on the same curve, almost within the limits of experimental error.

To find the form of $f(T)$ which agrees most closely with the observations, we write equation (6) in the form

$$\left(\frac{\lambda}{\sin\theta_1}\right)^2 \log_e \frac{R_T}{R_1} = -bf(T)\left(\frac{\sin\theta}{\sin\theta_1}\right)^2 + \text{const.} \quad . \quad (8)$$

Thus, if $\left(\frac{\lambda}{\sin\theta_1}\right)^2 \log \frac{R_T}{R_1}$ is plotted against $f(T)\left(\frac{\sin\theta}{\sin\theta_1}\right)^2$, all the points should lie on the same straight line, whatever the order of the spectrum observed, and whatever the wave-length. Debye's theory indicates that $f(T)$ should be proportional to T, but if $\log \frac{R_T}{R_1}$ is plotted against T, not even an approximately straight line is obtained. If, however, we plot $\left(\frac{\lambda}{\sin\theta_1}\right)^2 \log \frac{R_T}{R_1}$ against $T^2\left(\frac{\sin\theta}{\sin\theta_1}\right)^2$, all the 33 experimental points lie very nearly indeed on a straight line. This curve is shown in fig. 2, where the circles, triangles, squares, and crosses correspond to those in fig. 1.

Fig. 2.



The fact that all the points lie on the same line means that the exponent of the Debye factor is proportional to $\frac{\sin^2\theta}{\lambda^2}$

for all the spectra investigated; while the fact that a straight line is obtained when $f(\mathrm{T})=\mathrm{T}^2$ means that we can write the factor

$$e^{-b\mathrm{T}^2\frac{\sin^2\theta}{\lambda^4}}.$$

Calculating, by the method of least squares, the most probable straight line in fig. 2, we obtain

$$\mathrm{R}_\mathrm{T} = \mathrm{R}_0 e^{-1{\cdot}162\times10^{-5}\frac{\sin^2\theta}{\lambda^2}.\mathrm{T}^2},$$

where λ is expressed in Ångström units, as the empirical expression which fits the experimental results most closely.

8. We have seen that, according to the theoretical work of Debye, the exponent M in the temperature factor should be given by

$$-\mathrm{M} = \frac{6h^2}{\mu k\Theta}\sin^2\theta\,\frac{\phi(x)}{x},$$

where $x=\frac{\Theta}{\mathrm{T}}$, and Θ is the "characteristic temperature" which for rocksalt is 280° absolute. For values of T small compared with Θ this reduces, according to Debye, to

$$-\mathrm{M} = \frac{\pi^2h^2}{\mu k\Theta^3}\,;\,\frac{\sin^2\theta}{\lambda^2}\mathrm{T}^2\,; \quad . \quad . \quad . \quad . \quad . \quad (9)$$

while for high temperatures

$$-\mathrm{M} = \frac{6h^2}{\mu k\Theta^2}\,\frac{\sin^2\theta}{\lambda^2}\,.\mathrm{T}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The experimental results show that M is actually proportional to $\frac{\sin^2\theta}{\lambda^2}$, and this would appear to indicate that the observations are reasonably accurate, and also that the allowance for general radiation has been made correctly, for the proportion of general to characteristic radiation is very different for the different spectra examined, and different also for the same spectra in the case of rhodium and molybdenum radiations.

But the results do not agree in the least with theory as to the form of the function of the temperature contained in M. Over the range of temperature considered, M should be proportional to T, whereas the results showed that with a fair degree of accuracy it is proportional to T^2, which according to the theory should only be the case for temperatures up to about 50° absolute.

For high temperatures the form of M is the same as that obtained in the elementary treatment, from which

$$-M = \frac{16\pi^2 k}{f} \frac{\sin^2\theta}{\lambda^2} T,$$

where f is the force called into play when the atom is displaced by unit distance from its equilibrium position. Comparison shows then that

$$\frac{f}{\mu} = \frac{8\pi}{3} \frac{k^2}{h^2} \Theta^2,$$

or that the restoring force f is proportional to the square of the characteristic temperature.

If we take

$\Theta = 280°$,
$h = 6{\cdot}55 \times 10^{-27}$ erg. sec.,
$k = 1{\cdot}39 \times 10^{-16}$,
$\mu =$ average mass of an atom in the structure
$= 4{\cdot}85 \times 10^{-23}$ gm.,

we obtain for the case applicable to high temperatures

$$-M = 4{\cdot}89 \times 10^{-3} \frac{\sin^2\theta}{\lambda^2} . T, \quad . \quad . \quad . \quad (11)$$

λ being expressed, as before, in Ångström units. For (300) this reduces to

$$-M = 1{\cdot}39 \times 10^{-3} T. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

TABLE II.

T.	$\frac{R_T}{R_1}$ (calc.).	$\frac{R_T}{R_1}$ (obs.).
300°	·973	·98
400°	·846	·79
500°	·735	·60
600°	·640	·42
700°	·558	·27
800°	·486	·17
900°	·422	·10

Table II. shows the values of $\frac{R_T}{R_1}$ calculated from this formula compared with those actually observed. It is evident that the intensity of the spectrum falls off far more rapidly with increasing temperature than theory indicates. The difference between the observed and calculated figures is much greater than could be accounted for by experimental errors, and there must therefore be some factor which diminishes the intensity as the temperature rises which has not been allowed for in the theory.

One possibility which might be worth examining is that the value of the factor F may depend on the temperature. The theory treats the atoms as diffracting points. Now we know that the atom does not diffract even approximately as a point, particularly for large values of θ. The electrons are distributed around the atomic nuclei throughout a region whose dimensions are comparable with the spacing of the crystal planes; this causes a rapid decrease in the effective scattering power of the atom as it increases, and the factor F is introduced to allow for this. If, owing to the temperature vibration and the consequent jostling of atom against atom, the electron orbits were caused to vibrate about their mean positions, this would cause a change in the factor F in such a direction as to increase the falling-off of intensity with temperature.

Another possibility, although it seems very unlikely that it could account for such a large effect as that observed, is that the crystal may become softer as the temperature rises, so that an atom is more easily displaced from its position of rest. This would be equivalent to supposing that the characteristic temperature Θ depends on the temperature—an hypothesis which might be investigated by examining the Reststrahlen at different temperatures. To account for the T^2 law on this hypothesis alone, it would have to be assumed that Θ varied as $\frac{1}{\sqrt{T}}$. This seems highly improbable, and it is more likely that several factors work together and produce, over the range of temperature used, a law approximating closely to the T^2 law.

It is evidently desirable to extend the measurement to low temperatures, and experiments by means of which it is hoped to measure the intensity of reflexion at liquid-air temperature are already in progress.

Another point to be noticed is that in rocksalt we have two different kinds of atom—sodium and chlorine. In all the spectra so far examined we are dealing with the sum of the contributions from Na and Cl. In the case of spectra such as (111), (333), (311), (555), and so on we are, however, dealing with the difference of the contributions from

Na and Cl. It is proposed, therefore, to make a set of observations using the (333) spectrum, in order to see whether the law still holds good in this case.

In conclusion, I wish to express my thanks to Professor W. L. Bragg, F.R.S., for his interest and advice during the course of the work, and to Mr. W. A. Wood, B.Sc., for help with a number of the observations. My thanks are also due to Mr. W. Kay and Mr. W. Reynolds for much assistance in the design and construction of the apparatus. The X-ray bulb used in this research was very kindly presented to the laboratory by the General Electric Company of Schenectady, New York, and the alternator was purchased with the aid of a grant made by Messrs. Brunner Mond, Ltd.

Summary.

1. A series of measurements of the intensity of reflexion of X-rays from the (100) face of a rocksalt crystal at temperatures between 19° C. and 650° C. are described. The spectra investigated were the 2nd, 3rd, and 4th orders, using molybdenum Kα radiation, and the 3rd order, using rhodium Kα radiation.

2. A theoretical formula obtained by Debye shows that if R_T is the intensity of a spectrum reflected at a glancing angle θ at absolute temperature T; R_0 that at absolute zero:

$$R_T = R_0 e^{-bf(T)\frac{\sin^2\theta}{\lambda^2}} = e^{-M},$$

where b is a constant and $f(T)$ is some function of the temperature. The theory indicates further that over the range of temperature employed, M is of the form

$$-aT\frac{\sin^2\theta}{\lambda^2}.$$

3. The experiments show that M is proportional to $\frac{\sin^2\theta}{\lambda^2}$ for all the spectra investigated, but that instead of being proportional to T it is proportional to T^2. The results obtained may be expressed by the empirical formula

$$R_T = R_0 e^{-1\cdot162\times10^{-6}\frac{\sin^2\theta}{\lambda^2}T^2},$$

where λ is expressed in Ångström units.

The intensity diminishes as the temperature rises much more rapidly than theory indicates.

The University, Manchester,
Jan. 28, 1925.

LXV. *Adsorption from the Gas Phase at a Liquid-Gas Interface.*—Part III. *By* THOMAS IREDALE [*].

IN attempting to measure the surface tension of mercury in a vacuum by the drop method (Phil. Mag. xlviii. p. 189, 1924) certain difficulties were experienced owing to the rapid accumulation of impurities on the surface. In air, the surface tension was always higher than in a vacuum, except when it was measured with great rapidity in the vacuum, and also, in special cases, when the apparatus was newly cleaned and freshly-distilled mercury employed. It has been found very difficult to ascertain the exact nature of these impurities in every case, but it seems impossible now to believe in the suggestion originally made, that the anomalies observed are due to the presence of water films on the mercury surface. Difficulties of a similar kind have been experienced in the lubrication experiments of Hardy and co-workers (Phil. Mag. xxxviii. p. 32, 1919; Proc. Roy. Soc. A, c. p. 550, 1922), and are as likely as not due to adsorbed films, not necessarily derived from the vapour phase, which cannot be removed at ordinary temperatures even in the highest possible vacuum. In the washing and cleaning of glass apparatus with the usual reagents, certain impurities may sometimes be left behind on the glass which can only be removed by a more drastic method of rubbing or polishing of the glass surface. Such a procedure, however, would be very difficult with apparatus consisting of long capillary tubes, and this is probably one of the most serious defects in the original drop-weight apparatus designed by the author. The mercury column has to move against the interior glass surface of the capillary before issuing in drops from the orifice, and the chances of contamination in this way are very great. The possibility also of the electrification of the mercury by friction against the glass cannot entirely be ignored, but the earthing of the mercury in many instances has not changed the essential aspects of the phenomenon. It is remarkable that the presence of the air should so greatly hinder the adsorption of the impurities, but this does not seem to be a reversible effect; reversible, in the sense that the admission of air to a surface already formed in the vacuum does not appear to result in a desorption of the impurities. It must be admitted, however, that the technique of the drop method is not sufficiently adaptable to the measurement of such reversible effects. What is needed is some method of measuring the surface tension of mercury which can be applied to both old and new surfaces. We could find the tension from the contour of a surface formed in a vacuum, and note how it changed on admission of air. If the change in shape pointed to an increase in the tension, we would be justified in saying that the effect was a reversible one. But in the drop method, the drop usually detaches before the air can be properly admitted to the dropping chamber, owing to vibration and similar causes; and this technical imperfection makes it difficult to say what one is actually measuring in many cases. Such vibration may be induced by the surging of the gas molecules as the air fills the vacuous space, and the drop will always detach at the point of maximum instability. We should not be justified in saying, therefore, that the adsorption of the impurities was irreversible, as the growth of the drop might be hindered owing to other extraneous causes. The drop method, then, is at best a dynamical one, and cannot be employed for accurately measuring reversible adsorption effects.

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[*] Communicated by Prof. F. G. Donnan, F.R.S.

Another difficulty with the drop apparatus is the breaking apart of the mercury column in the capillary which is probably due to some minute speck of dust getting into the apparatus. In spite of every precaution the progress of the work was hampered a great deal owing to this cause.

Of other possible methods of measuring surface tension, that of the sessile drop seemed to meet the requirements most satisfactorily. It has recently been employed by Richards and Boyer (Journ. Amer. Chem. Soc. xliii. p. 274, 1921) for both mercury and liquid gallium, but was in use as far back as the time of Laplace. Quincke (*Ann. Physik*, cv. p. 38, 1858) was the first to make the most extensive use of the method, not only for mercury, but for a variety of other liquids, and seems to have made the first attempts to measure accurately the distance from the top of the drop to its maximum diameter. In the case of large drops this distance, h, is connected with the surface tension by the relation

$$h^2 \doteq a^2 = \frac{2\sigma}{\rho g},$$

ρ being the density of the liquid.

The most complete study of the forms of sessile drops of mercury is that of Bashforth and Adams ('An Attempt to test the Theories of Capillary Action': Cambridge University Press, 1883). Their method is to trace out successive small portions of the curve of the drop by means of the differential equation to the curve, "the increments of the coordinates being developed in series proceeding according to ascending powers of the increment of the quantity chosen as independent variable." The procedure is very long and tedious, but its accuracy is unquestioned. The most interesting result of their investigation is the relationship of the capillary constant *a*, the distance *h*, and the radius (maximum) of the drop.

From measurements made on their published diagrams and on reference to their tables, it is found that *h* gradually approaches the value of *a* (see Table I.) as the drop increases in radius from 1·9 mm. to 4 mm.

TABLE I.

Relationship of *h* and *a* for Drops of different Radii.
(Bashforth and Adams's tables.)

Radius of Drop.	*h*.	$\sqrt{\frac{2}{\alpha}}$.	$\sqrt{\frac{1}{\alpha}} = a$.
1·905 mm.	1·499 mm.		
2·515 ,,	1·854 ,,		
2·972 ,,	2·034 ,,		
3·353 ,,	2·134 ,,		
3·658 ,,	2·209 ,,		
3·990 ,,	2·235 ,,	3·167 mm.	2·241 mm.

It would not be satisfactory to employ drops less than 1 cm. in diameter, and in most of the experiments described in this paper the diameter was usually 1·5 cm. It is to be remarked, however, that the value of *a* computed from Bashforth and Adams's tables is exceptionally low—2·241 mm. Most experimenters have found values for *a* varying from 2·5 to 2·8 mm., and it is to be expected that these differences are due to varying degrees of contamination of the mercury surface.

Ferguson (Phil. Mag. xxv. p. 507, 1913) has deduced a relationship between *h* and *a* which is very similar to an equation originally given by Poisson ('*Nouvelle Théorie de* *l'action capillaire,'* p. 212), and involves a first-order correction of considerable magnitude. I do not know what to make of this equation, as it yields results nearly 25 per cent. lower than those calculated from the simple equation

$$h^2 = \frac{2\sigma}{\rho g}$$

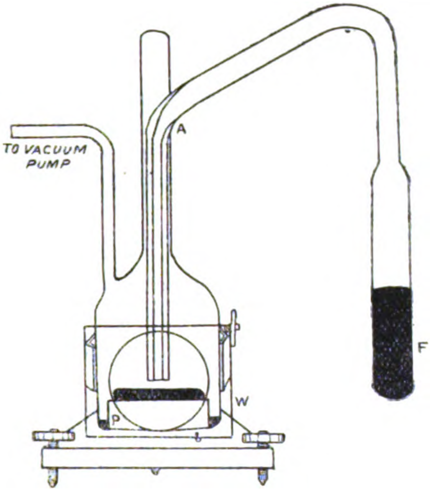
for drops 1·5 cm. in diameter; and these latter calculations are more nearly in agreement with the surface-tension values by the drop method. Now, the drop method has been shown to rest on at least an *experimentally* sound basis, and is hardly likely to give rise to an error as great as 25 per cent. In all the experiments described in this paper I have computed the surface tension with the aid of the simplified equation given above; and as the diameter of these sessile drops was 1·2–1·5 cm., some idea of the order of magnitude of the correction term can readily be formed by those who consider the correction necessary.

The use of very large drops is unnecessarily cumbersome, especially as the measured height h is found to have a constant value after a certain diameter is reached.

Most experimenters form a globule of mercury on a horizontal surface with the aid of a pipette, which is no doubt very thoroughly cleaned, but probably results in some inevitable contamination of the mercury surface. I have adopted a more satisfactory method of distilling over a quantity of mercury *in vacuo* on to a clean glass plate, a very small depression being made in the centre of the plate to assist the formation of the first portions of the globule. The procedure will be readily understood from fig. 1, and its success depends on the form of the curvature of the capillary tube at A. If the distillation is carried out properly and the glass surfaces are absolutely clean, the small globules of mercury should roll over the surface and pass down the capillary without clogging at A. The chances of surface contamination are minimized in this way, but too great emphasis cannot be laid on the necessity for rigorous cleaning of all portions of the glass that are likely to come into contact with the mercury. The apparatus should be treated with hot chromic acid, with nitric acid and alcohol, and also, if necessary, with pure boiling alcohol for some time. This applies more especially to the glass plate on which the mercury globule rests. Such treatment, however, may not always remove all the impurities adhering to the surface. Gas films and water films may have to be removed by outgassing the apparatus at high temperatures, but there are reasons now for believing that such films are only of secondary importance so far as contamination of the surface is concerned.

Observations of the drop were made with a cathetometer through the window W of plane, optical glass cemented on to a circular opening in the main chamber of the apparatus. No satisfactory cement made of inorganic materials was found which could be used with high vacua. A variety of red sealing-wax worked fairly well; it should be put on at a temperature of 110° C. The wax should not be heated too much, otherwise vapours will be given off which will foul the interior of the chamber. If necessary, the interior must be re-cleaned, with the window cemented in position. The experimental conditions would be very much improved if such adhesives could be done away with. After some time impurities from the wax undoubtedly creep over the surface of the glass, and the apparatus has to be taken to pieces and re-cleaned from time to time.

Fig. 1.



An accurate cathetometer made by the Cambridge and

Paul Instrument Co. was used to measure the dimensions of the drop, the outline of which was brought into focus by the telescope of the cathetometer against a strongly illuminated background. In locating the maximum diameter of the drop, I have adopted the method of Richards and Boyer (*loc. cit.*). A small filament lamp was lit some distance behind the telescope and on the same level with it. The lamp was reflected from a point on the maximum diameter as a tiny spot of light, which could be brought to a focus and located with fair accuracy by the cross-hairs of the telescope. The distance h in mm. from the top of the drop to the maximum diameter is given in the tables to one in the third place of decimals, as it is usually the average of a number of readings; but the order of accuracy is probably about $\pm 0{\cdot}0005$ mm. Richards and Boyer (*loc. cit.*) quote some of their results to one in the fourth place, and attribute the great variation in the value of h for different drops of mercury to the difficulty of adjusting optical conditions to perfect uniformity. I am inclined to think that the variations are too great to be due to this cause alone, and it is more likely that they are the result of variable contamination of the surface.

Reversible and Irreversible Adsorption at a Mercury Surface.

In carrying out the determinations with the apparatus described, the whole system is evacuated for some hours to a pressure of 10^{-5} mm. or less with the aid of a mercury-vapour pump. The mercury is then carefully distilled from the flask F to form a globule of the necessary dimensions on the plate P. It very often, though not invariably, happens that the surface tension of the first globule formed is very low, but it continues to rise as successive quantities of mercury are distilled over to form new globules. It appears as though the first portions of mercury removed some impurity from the glass surface; but sometimes the tension tends to fall slightly again on distilling further quantities of mercury. Some results of a typical experiment of this kind are given in Table II.

TABLE II.

Temperature 19°·5 C.

Successive drops No.	*h.* (mm.)	Surface tension. (dynes per cm.)
1	2·545	430
2	2·584	444
3	2·570	439
4	2·580	442
5	2·618	455
6	2·610	453
7	2·625	458
8	2·634	461
9	2·665	472
10	2·634	461
11	2·645	465
After remaining for twenty-four hours in the vacuum:		
	2·590	446
Dry, purified air admitted at 760 mm. After one hour:		
	2·588	445
More mercury distilled at 10^{-5} mm., after re-cleaning apparatus:		
1	2·580	442
2	2·587	445
Unpurified air from laboratory admitted. After 5 minutes:		
	2·534	427
After one hour:		
	2·485	410
Apparatus re-evacuated to 10^{-5} mm.:		
	2·490	412

The admission of pure dry air to a mercury surface formed in a vacuum does not appear to alter its tension very much, but the chances of contamination from the ordinary air of the laboratory are very great. The tension falls to a very low value, and does not rise again on re-evacuation of the system. The contamination in this case is completely irreversible. The effect of raising the surface tension by shaking or vibrating the drop, a phenomenon noted especially by Quincke, is only of a temporary nature, and the drop settles down to its original condition in a very short time. The vibration may temporarily disturb the orientation of the molecules of the adsorbed impurities, but it is evident that they cannot be made to leave the surface, even under very high vacua.

In extreme cases the tension has fallen by irreversible contaminatiom to as low a value as 296 dynes per cm. ($h=2{\cdot}110$ mm.). I have frequently observed that whenever it is found impossible by reason of the dirtiness of the apparatus to form drops with high surface tensions, the surfaces very quickly become contaminated, with a progressive fall in the tension.

These results are in harmony with those obtained by the drop method. When a surface is formed in air at atmospheric pressure, the presence of the air may hinder the adsorption of the impurities, but the admission of air to a surface already formed in a vacuum does not appear to result in a desorption of the impurities. In fact, it seems to have a slight lowering effect on the tension, and sometimes, if not purified, it may reduce it to a much lower value than was possible in the vacuum under the given conditions.

The view has been held that liquid mercury is composed of different sorts of complex molecules, and that changes in its surface tension with time are due to the slow accumulation at the surface of those modifications possessing the lower tension (see Bancroft, 'Applied Colloid Chemistry,' p. 134, 1921). The experiments described in this paper do not substantiate this argument. Moreover, we have evidence from another source (Smits, *Zeitsch. Physik. Chem.* lxxvii. p. 378, 1911) that mercury behaves as a unary substance.

It is impossible to believe that the contamination of the surface is due to water vapour adsorbed from the glass as originally suggested. I have taken a globule of mercury with a clean surface (tension about 470 dynes per cm.), and exposed it to water vapour up to the saturation pressure (temperature 20°·5 C., pressure 18 mm.). The results were not very interesting, as the effect of water vapour on the tension is rather small :

Pressure of water vapour. (mm. Hg.)	h. (mm.)	Surface tension. (dynes per cm.)
13·5	2·610	453
18·0	2·597	449

These figures, however, are in fairly good agreement with those obtained by the drop method (Phil. Mag. xlviii. p. 180, 1924), using an air-water vapour mixture. But it has not been found possible to condense the water on to the mercury surface at the saturation pressure. By slightly warming the bulb containing the water with the hand, the water readily condenses on the walls of the apparatus, but there is no change in the tension of the mercury. In the drop-weight experiments, the mercury surface was formed very near to the water surface, and in this vicinity momentary conditions of super-saturation might prevail, favourable to the rapid condensation of the water. The theoretical aspects of this phenomenon, however, are discussed in a later part of this paper.

Further adsorption experiments have been carried out with the vapours of certain organic liquids, no admixture with air being allowed in these cases. The liquids were contained in small bulbs communicating with the apparatus and kept at various temperatures to give vapours of different pressures. The apparatus was first of all exhausted to a presure below 10^{-5} mm., a satisfactory globule of mercury formed by distillation, and after shutting off this part of the system from the pumps the vapour of the organic liquid was allowed to enter the chamber containing the globule. The pressure of the vapour was recorded by a mercury manometer, and could be varied within certain limits by shutting off the vapour from the liquid supply and expanding it into the main part of the system. The reversibility of the adsorption could be tested by this means, as changes in the shape of the globule could be observed as the vapour pressure was first increased and afterwards reduced to its original value. As the temperature coefficient of the surface tension of mercury is not very large, it sufficed for the present purpose to work in a room of fairly constant temperature.

Table III. records some results with the vapour of benzene, which indicate that the adsorption is a partly reversible phenomenon. But it seems practically impossible to remove the last traces of vapour from the surface. These data are expressed graphically in fig. 2, and the points marked with squares are those which were obtained by reducing the pressure to its original value after reaching the saturation point. They mark the limits of reversibility of the process.

The results are in fair agreement with those previously obtained by the drop method, using air-vapour mixtures, and, as will be shown later, give much the same value for the area per molecule of adsorbed benzene on the mercury surface.

Fig. 2.

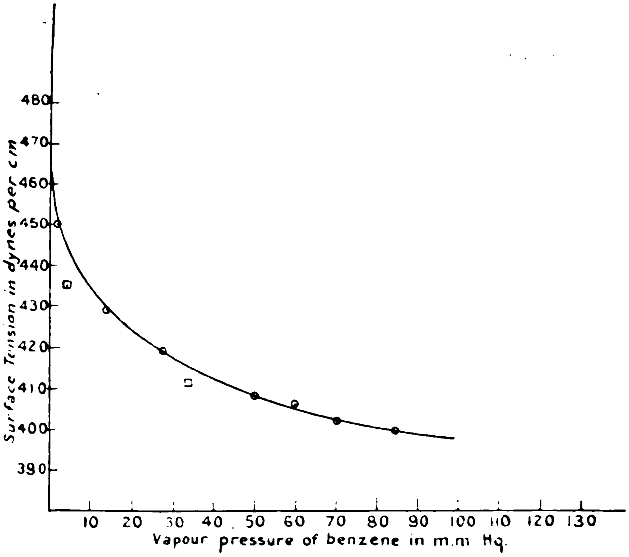


TABLE III.

Surface-tension Changes in Benzene Vapour.
Temperature 23° C.

Pressure. (mm. Hg.)	*h*. (mm.)	Surface tension. (dynes per cm.)
2·0	2·600	450
14·0	2·540	429
27·5	2·512	419
50·5	2·479	408
60·0	2·473	403
70·0	2·458	402
84·5	2·450	399
Brought back to:		
33·5	2·488	411
4·0	2·560	435
10^{-5}	2·558	434

I have obtained some remarkable results with a sample of benzene of doubtful purity which are recorded in Table IV. The adsorption in this case appears to be completely irreversible; but it is difficult to put any interpretation on these results, as we do not know how much this effect may be due to traces of sulphur compounds in the benzene.

[illegible]

TABLE IV.

Irreversible Changes of the Tension in Benzene Vapour. Temperature 21° C.

Pressure. (mm. Hg.)	*h.* (mm.)	Surface tension. (dynes per cm.)
33·0	2·473	406
51·0	2·352	368
73·5	2·227	330
Brought back to:		
1·0	2·228	330
After 20 minutes:	2·145	306

On re-evacuating to 10^{-5} mm. and continual shaking of drop, *h* rose to 2·510, and rapidly fell again to 2·177.

I have not followed up this phenomenon any further at present, but have observed that sometimes an irreversible contamination may take place concurrently with the adsorption of the vapour, and that this contamination is not necessarily derived from the vapour. It is safer to start with a clean surface of mercury and observe it for some time before admitting the vapour, so as to be certain that it is not being progressively contaminated in the vacuum itself.

The results of experiments with ethyl alcohol are recorded in Table V. and fig. 3, and with propyl chloride and ethyl

TABLE V.

Surface-tension Changes in Ethyl Alcohol Vapour. Temperature 21° C.

Pressure. (mm. Hg.)	*h.* (mm.)	Surface tension. (dynes per cm.)
1·0	2·605	451
8·5	2·570	439
12·0	2·555	434
17·0	2·540	429
26·5	2·522	423
47·0	2·498	415
Brought back to:		
2·0	2·570	439

Fig. 3.

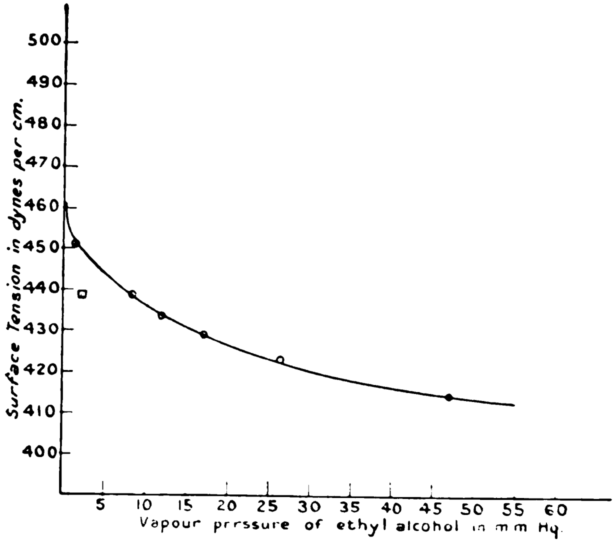
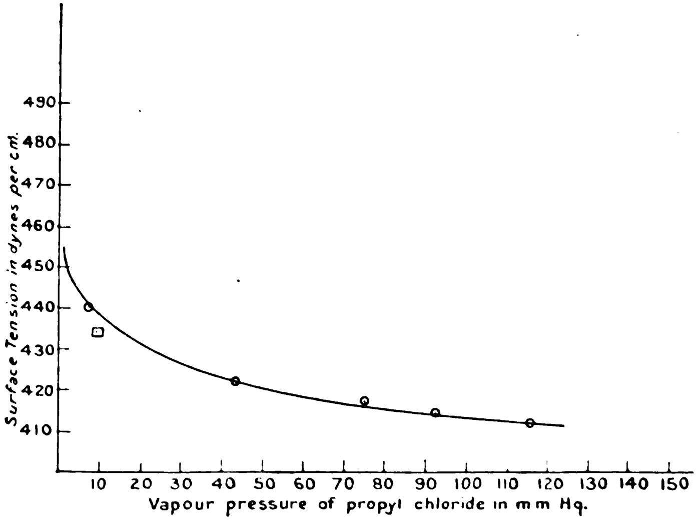


Fig. 4.



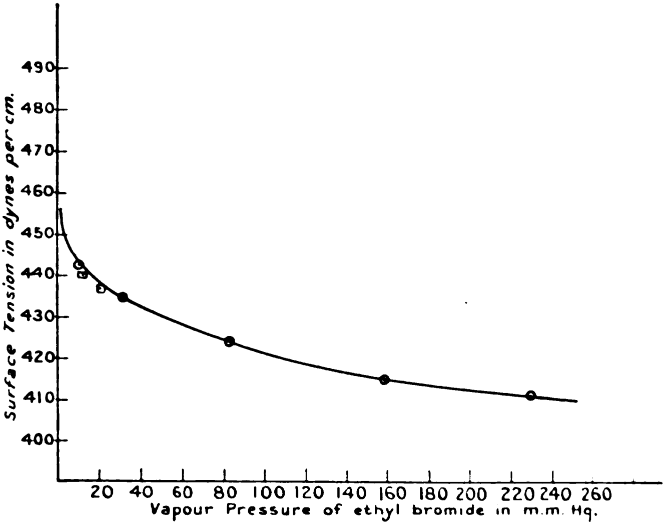
bromide in Tables VI. and VII. and figs. 4 and 5 respectively. As in the case of benzene, the adsorption of these substances appears to be within certain limits a reversible phenomenon. It is remarkable that these substances, which are more definitely polar than benzene and, especially in the

TABLE VI.

Surface-tension Changes in Propyl Chloride Vapour.
Temperature 21° C.

Pressure. (mm. Hg.)	*h*. (mm.)	Surface tension. (dynes per cm.)
7·0	2·575	440
43·5	2·519	422
75·0	2·505	417
93·0	2·492	413
116·0	2·485	411
Brought back to:		
9·0	2·555	434

Fig. 5.



case of the alkyl halides, possess an atom or group more likely to form a definite linking at the mercury surface, should have no more marked effect on the surface tension than benzene itself.

TABLE VII.

Surface-tension Changes in Ethyl Bromide Vapour.
Temperature 22° C.

Pressure. (mm. Hg.)	*h.* (mm.)	Surface tension. (dynes per cm.)
10·0	2·580	442
31·5	2·559	434
82·5	2·527	424
158·0	2·495	414
230·0	2·480	411
Brought back to:		
20·0	2·565	437
11·0	2·575	440

In the case of methyl iodide, however (Table VIII. and fig. 6), a very decided change in the nature of the adsorption was observed. Not only was the tension lowered to a much greater extent, but the adsorption appeared to be completely irreversible. [illegible]

TABLE VIII.

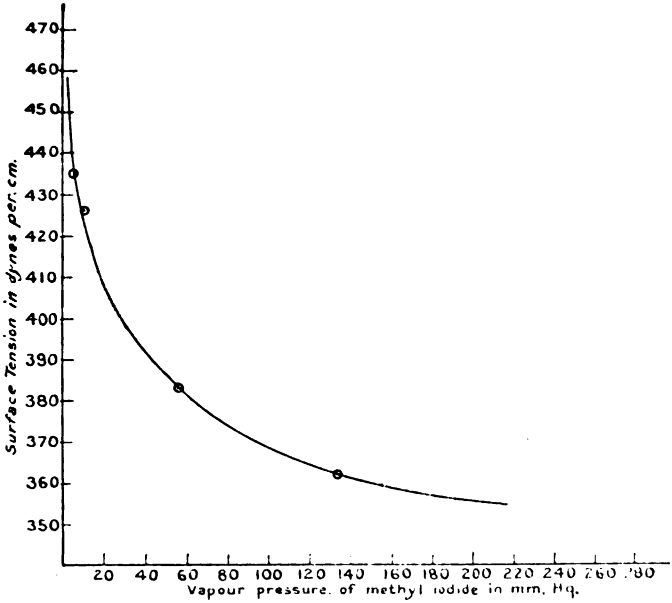
Surface-tension Changes in Methyl Iodide Vapour.
Temperature 22° C.

Pressure. (mm. Hg.)	*h.* (mm.)	Surface tension. (dynes per cm.)
4·5	2·560	435
10·5	2·531	426
56·0	2·400	383
134·0	2·335	362
Brought back to:		
7·0	2·335	362

(No increase in the tension on re-evacuation to 10^{-5} mm.)

Now mercury is known to form—at least in sunlight—a definite chemical compound with methyl iodide (Frankland, *Annalen*, lxxxv. p. 361, 1853; Whitmore, 'Organic Compounds of Mercury,' p. 89, 1921), and it is possible that the molecules of this substance are held at the mercury surface with a much greater tenacity than in the case of the other halides. This might be regarded as a low temperature analogue of an interesting phenomenon occurring at high temperatures—the irreversible adsorption of oxygen by tungsten studied by Langmuir (Journ. Amer. Chem. Soc. xxxv. p. 105, 1913; *ibid.* xxxviii. p. 2272, 1916). The oxygen atoms, however, are not regarded as forming a definite oxide at the tungsten surface, but rather some form of stable adsorbed film, in which the valency bonds of the oxygen atoms are fully saturated; but the valencies of the tungsten atoms on the surface are still partially saturated by union with the atoms in the layer beneath. It might be possible to apply a similar reasoning to the methyl iodide case, and this will be discussed presently in dealing with the space taken up by the molecules on the mercury surface.

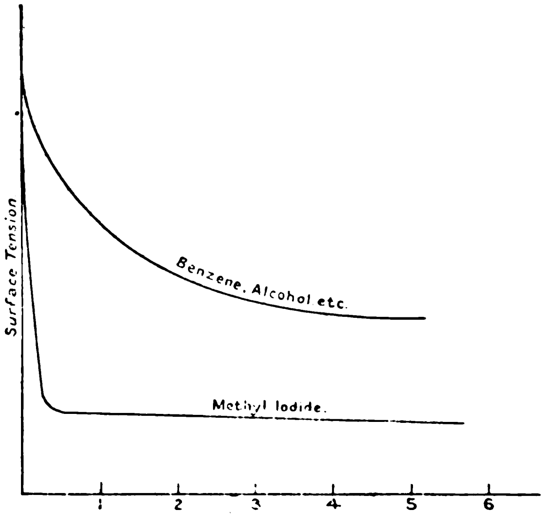
Fig. 6.



A definite surface compound would be quite a different thing from the average adsorption film held at the surface by secondary valence forces, which may be likened to a kind of surface solution. In the above case, the methylmercuric iodide may have a definite dissociation pressure of its own; but it must be noted that we reach the adsorption maximum along a curve very similar to that of any of the other substances which show reversible adsorption.

This brings up the interesting question of the rate of adsorption, as it might be thought that at low pressure the process was a very slow one, and that equilibrium was not always reached under the given experimental conditions. I have given some curves (fig. 7) to show how quickly the surface tension falls with time; but this is only an approximation, as it is a very difficult matter to measure the tension when it is changing so rapidly, owing to the impossibility of making the necessary optical adjustments within the short space of time required. I have observed, however, that for moderately high vapour pressures, 40–50 mm., the adsorption of the methyl iodide is much more rapid than that of any of the other substances examined. The rate of desorption in the reversible process seems to be quite as rapid as the adsorption itself; but this part of the technique of the method will have to be improved considerably before any reliable results can be expected.

Fig. 7.



Fall of surface tension with time.

It has been said that the tension may sometimes continue to change with time quite independently of the vapour. I have often observed, however, that after the mercury surface has been in contact with the vapour for an hour or more, the tension was very little different from what it was at the end of the first five minutes. It may safely be said that the adsorption equilibrium is reached in every case within a few minutes.

Purity of Materials.

The benzene was Kahlbaum's "Thiophen frei," and was redistilled after standing over phosphoric oxide.

The ethyl alcohol was practically anhydrous. It gave a negative test with a crystal of potassium permanganate, and was free from aldehydes as indicated by the silver nitrate test. The presence of traces of other homologues was not thought likely to be objectionable in the present experiments.

The methyl iodide was purified by shaking with dilute alkali, drying over calcium chloride, and distilling, the major portion boiling at 42°·5 C. (760 mm.) being collected. It was redistilled from silver-foil, and kept over a small quantity of silver in an amber-coloured bottle. The bulb of the apparatus containing the methyl iodide was shielded from the light during the experiments.

The ethyl bromide and propyl chloride were Kahlbaum's pure chemicals, and were used immediately after opening the sealed bottles.

Methods of Calculating the Adsorption.

In the previous paper of this series (Phil. Mag. xlviii. p. 187, 1924) reference was made to the difficulty of calculating the amount of the saturated adsorption owing to the form of the σ-p curve. It so happens in most of these instances that the surface tension is some logarithmic function of the pressure, so that the value of $\frac{d\sigma}{dp}$ does not always afford a convenient means of calculating the adsorption coefficient Γ.

It is possible to express these relationships in the form of an equation very similar to Szyskowski's (*Zeitsch. Physik. Chem.* lxiv. p. 385, 1908), which Langmuir has made use of

(Journ. Amer. Chem. Soc. xxxix. p. 1885, 1917) to calculate the adsorption coefficient in a number of instances. I have thought it worth while to re-calculate the values for the saturated adsorption of benzene and methyl acetate with the aid of this derived form of Szyskowski's equation, and to compare them with the previous values obtained by the use of the tangent to the σ-p curve.

Inserting vapour pressure for concentration in the original Szyskowski equation, we have:

$$\frac{\sigma}{\sigma_0} = 1 - \mathrm{B} \log\left(\frac{p}{\mathrm{A}} + 1\right),$$

where σ_0 = surface tension of mercury,
σ = surface tension for any particular vapour pressure p ...,
B & A are constants.

Langmuir (*loc. cit.*) has shown that, by differentiating this equation and comparing it with the Gibbs adsorption equation, the limiting amount of adsorbed vapour will be expressed by:

$$\Gamma = \frac{0{\cdot}434\,\mathrm{B}\sigma_0}{\mathrm{RT}}$$

in gram molecules per square centimetre.

Now, in finding the value of the constant B, I have adopted the original method of Szyskowski. To values of $\frac{\sigma}{\sigma_0}$ differing by constant increments, I have found corresponding values of σ and p from the smoothed σ-p curve; Δp are the successive increments of p, and $\frac{\Delta p_{n+1}}{\Delta p_n}$ their ratios (R). If the logarithmic law be followed, R should be a constant; and it appears to be so within the limits of accuracy of Szyskowski's own data on which Langmuir bases his general conclusions. Now, if n be the number of successive increments of $\frac{\sigma}{\sigma_0}$, and d the value of this increment,

$$\mathrm{B} = \frac{nd}{n \log \mathrm{R}} = \frac{d}{\log \mathrm{R}}.$$

TABLE VIII. (*a*).

$\frac{\pi}{\sigma_0}$.	σ.	p.	Δp.	$\frac{\Delta p_{n+1}}{\Delta p_n}$
0·840	396·5	72·0		
			17·0	
0·850	401·2	55·0		
			12·2	(1·40)
0·860	405·9	42·8		
			9·1	1·34
0·870	410·6	33·7		
			7·5	1·22
0·880	415·4	26·2		
			6·0	1·25
0·890	420·1	20·2		
			4·5	1·33
0·900	424·7	15·7		
			3·4	1·32
0·910	429·4	12·3		
			2·6	1·30
0·920	434·2	9·7		
			2·1	1·24
0·930	438·9	7·6		
			1·7	1·24
0·940	443·6	5·9		
			Mean (R)	1·28

Hence

$$B = \frac{0{\cdot}01}{\log 1{\cdot}28} = \frac{0{\cdot}01}{0{\cdot}1092} = 0{\cdot}0961,$$

so that

$$\Gamma = \frac{0{\cdot}434 \times 0{\cdot}0961 \times 472}{8{\cdot}4 \times 10^7 \times 299}$$

$$= 0{\cdot}078 \times 10^{-8} \text{ gram molecule per sq. cm.}$$

$$= 0{\cdot}0473 \times 10^{16} \text{ molecules per sq. cm.}$$

$\therefore$ area per molecule $= 21{\cdot}2 \times 10^{-16}$ sq. cm. ;
previously found value $= 21{\cdot}0 \times 10^{-16}$ sq. cm.

From the data obtained with methyl acetate it is found in a similar way that

$$B = 0{\cdot}0715,$$

$$\Gamma = 0{\cdot}0583 \times 10^{-8} \text{ gram molecule per sq. cm.}$$

$$= 0{\cdot}035 \times 10^{16} \text{ molecules per sq. cm.}$$

$\therefore$ area per molecule $= 28 \times 10^{-16}$ sq. cm. ;
previously found value $= 27 \times 10^{-16}$ sq. cm.

The agreement between the values calculated by the two methods may be considered as satisfactory.

The adsorption coefficient has also been calculated from the data on the lowering of the surface tension of the sessile drop. The results obtained by this method are not likely to be of the same order of accuracy as those computed by the drop method; but in the case of benzene the agreement is fairly satisfactory.

Γ was found to be $0{\cdot}0726 \times 10^{-8}$ gram molecule per sq. cm., giving an area per molecule on the surface of 23×10^{-16} sq. cm., which is a little larger than the previously found value.

For ethyl alcohol, $\Gamma = 0{\cdot}0567 \times 10^{-8}$ gram molecule per sq. cm., and the area per molecule, 29×10^{-16} sq. cm. It is interesting to compare this with the value found for the area (29×10^{-16} sq. cm.) from the data of Bircumshaw (Journ. Chem. Soc. cxxi. p. 887, 1922) on the surface tension of water-ethyl alcohol mixtures. The agreement is striking, but it is doubtful if the results are strictly comparable. In the case of substances adsorbed on the surface of water, it is usual to imagine some form of solubility such as affects the polar group of the molecule. With the mercury surface this assumption would not be feasible. We must imagine some kind of linking of the atoms at the surface, whereby the area per molecule of adsorbed substance is determined partly by the specific group attached to the surface, but more especially by the spacing of the mercury atoms themselves. In connexion with this there are some crystallographic data (McKeehan and Cioffi, Phys. Rev. xix. p. 444, 1922; Debierne, *Comptes Rendus,* clxxiii. p. 140, 1921) from X-ray examination of both solid and liquid mercury, but they are not considered satisfactory (Wyckoff, 'Structure of Crystals,' p. 243, 1924). It is noteworthy, however, that the molecule of methyl iodide appears to accupy only about half or a third the space appropriated by the molecules of the other substances (Table IX.). Now it is fairly certain that the formula of methyl-mercuric iodide is $CH_3—Hg—I$. If we imagine that this compound is actually formed at the mercury surface, and that with the saturated adsorption all the available spaces of the surface are covered, then every

TABLE IX.

	Area per molecule in sq. cm. $\times 10^{16}$.
Methyl acetate	27·5
Benzene	21 23
Ethyl alcohol	29
Propyl chloride	ab. 40
Ethyl bromide	ab. 40
Methyl iodide	13

mercury atom will be united by two bonds to the methyl group and the iodine atom respectively. But such an arrangement might not satisfy at the same time our idea of the electronic configuration of the system, and it would be better, from the analogy of the oxygen atoms on the tungsten surface, to imagine the methyl group and the iodine atom as each attached to a separate mercury atom, which is itself partially saturated by union with a mercury atom in the layer beneath. The area for each mercury atom on the surface will then be $6{\cdot}5 \times 10^{-16}$ sq. cm. It is evident that the molecules of the other substances are not packed so closely at the surface, nor are they held there with such tenacity; but it is not proposed to discuss this matter any further until more extensive data, particularly on the heats of adsorption, are obtained.

General Theory of Adsorption and Condensation.

It has been necessary in all these cases to postulate in the first instance the existence of a monomolecular film, and afterwards to calculate on this assumption the space appropriated by each molecule on the surface. But we might also suppose that only a small part of the surface is covered with the adsorbed molecules, and that there is a gradual decrease in the density of the vapour outwards from the surface through a layer several molecules thick. This assumption, however, would not be in accord with the usually accepted idea of the nature of molecular attractive forces, and certainly not in agreement with the very convincing theories of Langmuir and Harkins, based as they are on some very conclusive experimental evidence.

Now, the film of discontinuity imagined by Gibbs was an essentially different thing. In his day, and until quite recently, it was usual to regard such a film as forming, what Hardy termed, a composite surface. The tension of such a film formed from the saturated vapour would be written $\sigma_A + \sigma_{AB}$, where σ_{AB} is the interfacial tension of the film and the liquid beneath it, and σ_A the surface tension of the liquid composing the film, assuming also that the two liquids are mutually insoluble. The condition of the film as it thinned to molecular dimensions was largely a matter of speculation. Hardy's interesting experiments on the tension of composite surfaces (Proc. Roy. Soc. lxxxviii. p. 312, 1913), especially with reference to the spreading of certain liquids on water, did not reveal the essential difference between the film formed from the vapour and the thicker film formed by the spreading liquid. But it was obvious that certain substances would form very thin films by adsorption of the vapour by the water that normally would not spread on water. The tension of such thin films could not be $\sigma_A + \sigma_{AB}$, as this was greater than the surface tension of water, σ_B.

Now, Gibbs imagined ('Scientific Papers,' i. p. 235) that the saturated vapour of water would form a thick film on a mercury surface whose tension was equal to $\sigma_A + \sigma_{AB}$. He quoted some figures of Quincke, and indicated that if we knew the surface tension of mercury under different pressures of water vapour up to the saturation value, we could calculate the amount of water on the surface, and hence find the thickness of the film. Quincke's figure for the tension of mercury at 20° C. is 539 dynes per cm., and for $\sigma_A + \sigma_{AB}$ $81 + 417 = 498$ dynes per cm. If experiments had been carried out to determine the surface tension of mercury for intermediate pressures of water vapour, a nearly linear relationship between the pressure and the tension would have been found. The pressure and density of water vapour at 20° C. are 17·5 mm. Hg. and 0·0000174 gram per c.c. respectively. Hence

$$\Gamma = 0{\cdot}0000174 \times \frac{41}{1{\cdot}75 \times 981 \times 13{\cdot}6} = 3 \times 10^{-8} \text{ gram per sq. cm.}$$

the exact requirement for a monomolecular film.

Since the film was imagined to possess the properties of liquid water in mass, being in equilibrium with the saturated vapour, such a result would have been regarded as an anomaly, as it was in conflict with the theory of molecular dimensions; and the concept of a monomolecular film having the tension equal to $\sigma_A + \sigma_{AB}$ is something entirely novel, and would not have been considered as adequately representing the facts.

But in how many cases, it may be asked, other than water, is this relation true? I have given in Table X. some figures for σ_m, the tension of the monomolecular film in the saturated vapour, and for $\sigma_A + \sigma_{AB}$, and it will be seen that σ_m is usually somewhat greater than $\sigma_A + {}_{AB}$.

TABLE X.

	σ_A.	σ_{AB}.	$\sigma_A + \sigma_{AB}$.	σ_m.
Water	73	375	448	449
Methyl acetate	25	370	395	412
Benzene	28	354	382	395
Ethyl alcohol	22	364	386	415
Methyl iodide	35	304	339	349

(Some of these figures are taken from the data of Harkins and Grafton (Journ. Amer. Chem. Soc. xlii. p. 2543, 1920) on interfacial tensions.)

Now it has been shown very conclusively by Gibbs ('Scientific Papers,' i. p. 258) that the most stable film between two phases such as these, the vapour phase of the substance A and the liquid phase B, would have the tension $\sigma_A + \sigma_{AB}$, provided that $\sigma_A + \sigma_{AB} < \sigma_B$, which is certainly the case for these films on the mercury surface. Gibbs, however, did not consider the possibility of building up a film from successive layers of molecules, and unless we knew how the tension changed with each layer, we could not find out how σ_m approached the value $\sigma_A + \sigma_{AB}$; for in all real changes the diminution in free surface energy per gram molecule of adsorbed substance cannot be less than the external work required to condense the gram molecule from the vapour state.

But there are some special instances where it seems fairly certain that $\sigma_m = \sigma_A + \sigma_{AB}$. I refer to the interfacial tension of two liquids slightly soluble in one another. The relationship is known as Antonoff's law (Antonoff, *Journ. de Chim. Phys.* v. p. 372, 1907; Hardy, Proc. Roy. Soc. A, lxxxviii. p. 313, 1913), and expresses the fact that this interfacial tension is equal to the difference of the tensions of the two liquid phases. Reynolds (Trans. Chem. Soc. cix. p. 466, 1921) has adduced some experimental evidence in support of this law. Now, in the case of benzene and water, the tension of water saturated with benzene is the same as the tension in the saturated vapour of benzene, and is equal to σ_m. The tension of the benzene saturated with the water is very little greater than the tension of benzene itself, σ_A. According to Antonoff's law, $\sigma_m - \sigma_A = \sigma_{AB}$ or $\sigma_m = \sigma_A + \sigma_{AB}$. There are not sufficient data to enable one to say if this law is capable of universal application.

There must be some cases, of course, where $\sigma_m < \sigma_A + \sigma_{AB}$; and this is to be found when the vapours of certain saturated organic substances, such as carbon disulphide, lower the surface tension of water; but the substances themselves cannot spread on the water, since $\sigma_A + \sigma_{AB} > \sigma_B$.

With mercury, however, the experimental results have in many cases indicated a very great fall in the tension when the mercury surface is formed in the saturated vapour; and this fall occurs most rapidly when the mercury is near the surface of the other liquid. Owing to the slight temperature fluctuations of the thermostat, momentary conditions of supersaturation of the vapour may occur, favourable to a rapid condensation of the vapour in this vicinity; and it has been argued, with some justification, that the films formed in this way are of unusual thickness compared with the primary adsorption films. As far as changes in the tension are concerned, what must happen is this: with the primary adsorption of a monomolecular film, the drop registers a tension which is that of a composite surface and may be of the order $\sigma_A+\sigma_{AB}$. As each layer of molecules is added to the film to form a new and independent surface of the condensed liquid, the drop begins no longer to register the tension of the composite surface, but rather the interfacial tension σ_{AB}. But what concerns us most is the change, if any, in the orientation of the first layer of molecules adjacent to the mercury surface. It is impossible not to believe that some change has taken place, because the tension associated with this first layer has fallen from $\sigma_A+\sigma_{AB}$ to σ_{AB}. It seems reasonable, therefore, to assume that the molecules become more closely packed at the surface during the condensation process; but, if so, this change in the orientation must be due to an intermolecular attraction extending through a layer many molecules thick.

But as long as σ_m is of the order $\sigma_A+\sigma_{AB}$, condensation under isothermal conditions is thermodynamically impossible; and we must assume, as we have already done, that there is some slight degree of supersaturation of the vapour, in order that the condensation may take place. But a thick film already formed in this way and possessing the tension $\sigma_A+\sigma_{AB}$ would not be unstable under isothermal conditions unless $\sigma_A+\sigma_{AB}>\sigma_m$, in which case it would first break up into lenses and afterwards form the primary film of the tension σ_m. The difficulty of experimentation in these cases would lie in the accurate control of the temperature.

Now, the *interfacial* tension has been used in recent years as the basis of certain calculations of the attraction of one liquid surface for another. It occurs, for instance, in Dupré's equation, $W=\sigma_A+\sigma_B-\sigma_{AB}$, where W is a measure of the attractive forces, the adhesional work; and this has been used by Harkins (Journ. Amer. Chem. Soc. xxxix. p. 354, 1917) in the development of his theory of the orientation of molecules at liquid-liquid interfaces. But Harkins's deductions would lead us to believe that the *interfacial* tension of two liquids is the result of certain molecular rearrangements confined exclusively to the first layer of molecules. This can hardly be the case, as we have seen that the *interfacial* tension may result from an intermolecular attraction extending through a layer several, or many, molecules thick. His argument, at first sight, seems very convincing, but it is doubtful if his results can be interpreted in so simple a manner.

It is hoped shortly to be able to communicate some results of the direct measurement of the adsorption.

Summary.

It has been shown by two independent methods of measuring the surface tension of mercury, when the mercury surface is exposed to vapours of different pressures, that these vapours adsorb on the surface to give films that, in all probability, are only one molecule in thickness; and the space taken up by these molecules on the surface has been found to agree fairly satisfactorily with data of a similar kind from other sources.

In the saturated vapour, under special conditions, it has been found possible to form films which are of much greater thickness; but it has been argued on thermodynamical grounds that such condensation is impossible under strictly isothermal conditions, if the tension of these films is not less than the tension of the monomolecular films.

The mercury surface has been found to be very easily contaminated by traces of impurities, the source of which has often been difficult to ascertain; but it is possible that they are derived in part from the glass surfaces with which the mercury comes in contact, and are not readily removed by the usual cleaning agents. Such contamination is irreversible, and the adsorbed impurities cannot be removed at ordinary temperatures, even in the highest vacua.

The adsorption of the vapours of certain organic substances has been found to be largely reversible, except in the case of such a substance as methyl iodide, which is known to form a definite compound with mercury. It is considered that the bond of union between the mercury atoms and the halide molecules is of a more pronounced type than in the case of the molecules of other substances. It is suggested that a distinction may have to be drawn between a "surface compound" and a "surface solution," even in these simple cases.

The investigation of the adsorption of vapours on liquid surfaces is considered to open up a new and promising field for the study of adsorption films and molecular structure.

I am indebted to Professor Donnan for the great interest he has taken in this investigation, and to the Department of Scientific and Industrial Research for a grant of money which has enabled me to carry it out.

The William Ramsay Laboratories of
Inorganic and Physical Chemistry,
University College, London,
December 20, 1924.

LXVI. *Notices respecting New Books.*

The History of One Hundred Years of Life of the Leeds Philosophical and Literary Society. By Lieut.-Col. E. Kitson Clark, 1924. (Jowett & Sowry Ltd., Leeds.)

THIS very interesting and delightful volume chronicles the activities of one of the leading philosophical societies in the country. The Leeds Philosophical and Literary Society was founded in 1818, and has from that time pursued an honourable career. The writer of the volume has chosen the best possible way of commemorating the Centenary in reprinting selections from the actual Reports of the Society year by year. By skilful editing these extracts are made to tell the history of the Society, and indirectly they give a vivid picture of the intellectual interests of the more thoughtful citizens of Leeds during the century which is past.

The initial decision to purchase land and erect a building was made at a general meeting on May 7, 1817, and on July 9 the corner stone of the Court House was laid and a gold sovereign of 1817 and other coins were let in. The first meeting was held in the year 1819 to discuss a paper on "The Effects of Spirituous Liquors on the Human Frame." During the first ten years a great variety of subjects were discussed belonging to Archæology and History (24 meetings), Literature, Art, Pedagogy, and Ethics (54 meetings), Chemistry, Geology, Entomology (56 meetings), Physiology and Biology (18 meetings), Geography, Ethnography (11 meetings), and Economics (11 meetings). Many of the papers discussed have familiar titles. Thus in 1834 there was a discussion "On the general improvement and prosperity of Leeds as affected by the smoke of the factories." Others are not so familiar. Thus in 1848 the president read a paper on "The Principles of Education—for Professional Men, for Females, and for the Working Classes." It is interesting to notice the lecture on "The Colour of the Sky" by John Dalton, in 1828, and a lecture by Silvanus Thompson on "Waves of Sound and the Photophone," in 1880.

In 1840 it is recorded that "the tea and coffee for lectures were made exigible in the case of those only who arrived later than a quarter past seven, the hour of meeting being seven." The curve of unpunctuality varied correctly in inverse ratio to the severity of the penal regulations.

This is a fascinating volume, and if it stimulates others of the older societies of this type to a similar publication, will serve a purpose interesting not only to the professional scientific man.

La Technique du Vide. By L. Dunoyer. (Pp. 225. Paris, Les Presses Universitaires de France. 1924.)

This book provides a useful summary of the varied methods of producing and managing vacua. The subject has become of great importance during the past ten years, owing to its applications in the research laboratory, and in the technical production of lamps, valves, and X-ray tubes. The construction of mercury diffusion pumps is treated in some detail. Holweck's ingenious modification of the Gaede molecular pump will still be new to many people. The account of the many types of manometers, which have been proposed for the measurement of high vacua, serves to emphasize how unsatisfactory such measurements still remain.

Another section deals with the design of vacuum apparatus, the expulsion of occluded gases, etc. It is unfortunate that more information upon the making of glass to metal joints has not been included here. A short account is given of recent work on the disappearance of gases in the electric discharge.

The Earth, its Origin, History, and Physical Constitution. By HAROLD JEFFREYS, M.A., D.Sc., Fellow and Lecturer of St. John's College, Cambridge. (Cambridge University Press, 1924.)

THIS important volume is based to some extent on a set of lectures delivered by the Author in the University of Cambridge during the years 1920–1923. It is the first book in which any attempt has been made to present a *general* view of the present state of geophysics. It is a matter of great importance that a general survey of this kind should be made, and this work should mark a new era in the subject. Up to the present time the subject of geophysics has suffered very much from the fact that the problems with which it is concerned are of such extremely diverse kinds that it is impossible that any worker should have a specialist's knowledge of even a majority of them. And this state of affairs inevitably results in the independent development of different problems, even when the logical relation of the problems is intimate and important, and the feasibility of projected solutions of one can only be adequately evaluated by reference to the state of development of another, both as regards the data available and as regards the state of theorising with respect to it and the probability values to be attributed to the various theories.

In the present volume the desirability of coordinating the data and theory belonging to different problems is stressed at every possible opportunity; and for this reason the book is important also as an example of scientific method. And the matter of geophysics lends itself very readily to such treatment. For during recent years a remarkable feature of geophysics has been the extent to which different lines of attack have led to mutually consistent results. This is the more noteworthy when we take into consideration the very varied nature of the data on which geophysics as a science depends, and, more important still, the very varied nature of the hypotheses on which it depends. In part, however, these hypotheses are well established, as, for example, the laws of gravitation, heat conduction, radioactive disintegration, elasticity, and fluid friction.

The aim of the author has been to discuss the theories of the main problems of geophysics, and to exhibit their inter-relations. And throughout he has introduced quantitative and not merely qualitative comparison of theory with fact. A large number of the theories advocated have survived the test of quantitative application to several phenomena, while decent burial—with no necessity for any exhumation—has been given to many old favourites.

Such an object as quantitative testing necessarily entails the use of mathematics, and this will probably not make the book any easier for geologists nor prejudice them in its favour. But, as the author points out, "if geophysics requires mathematics, it is the earth that is responsible, not the geophysicist." The author has, however, been remarkably successful in making the spirit of his arguments intelligible to the non-mathematical reader, for he has on several occasions segregated the part of the argument which necessarily requires mathematical treatment, either open or veiled, and has given a clear statement of the point at which mathematics needs to be introduced and the point at which its use can be discontinued, and has, at the same time, recorded the mathematics for the sake of those who want them for reference. This treatment is plainly preferable to that of some writers, who endeavour by means of protracted discussion in words, to make intelligible to non-mathematicians arguments, which even the trained mathematician or logician requires to have in symbols.

We may conclude by recording our great admiration for the way in which this book has been constructed. It is the rôle of the scientist to take data of all kinds and build on them inductions and general laws. In geophysics, however, the task is especially difficult in view of the vast problems involved and the paucity of experimental, as opposed to observational data and, indeed, the relative paucity even of observational data in comparison with many sciences. The general principles of scientific method have, however, been applied in this book in a notable manner on material of very great interest, important parts of which are due to the insight and logical acumen of the author.

LXVII. *Intelligence and Miscellaneous Articles.*

THE INTERNATIONAL CRITICAL TABLES.

AT the meeting of the International Union of Pure and Applied Chemistry held in London in 1919, the American delegates submitted a proposal for the international compilation of critically prepared tables of the physical properties of chemical substances and technological materials. The proposal was approved by the Union, and the American National Research Council at Washington has since undertaken the financial and editorial responsibility for the undertaking. A Board of Trustees has undertaken to raise the sum of $200,000 or such part thereof as many be necessary. The editorial responsibility is invested in a Board of Editors, the

Editor-in-Chief being Dr. E. W. Washburn, formerly Professor of Physical Chemistry at the University of Illinois.

To ensure the international character of the Tables, Corresponding Editors have been appointed in the principal countries of the world. It may be added that the Tables are in no sense a commercial undertaking and the members of the Boards of Trustees and Editors and the Corresponding Editors serve in an honorary capacity.

The work of critically examining the data and of compiling the various tables is being carried out by well-known chemists, physicists, engineers, etc., some three hundred in number, who have been chosen for this purpose in the various countries of the world, largely on the basis of recommendations from the Corresponding Editors and their advisory committees.

These experts are not being expected to assume the responsibility of searching the literature, a task which is being carried out in the main by the editorial staff at Washington, but rather to assemble, to examine critically and to select the best value for each constant indicating at the same time the probable uncertainty.

Each portion of the Tables will be published over the name of the cooperating expert who has assumed responsibility for the selection, reliability and accuracy of the data in question. The size of each assignment has been restricted so that the work may be carried out within a reasonable time and without becoming too great a burden for any individual (or cooperating group of individuals) to bear.

The main language employed in the Tables will be English, but the introduction, table of contents, definitions, general explanatory text, and a very complete index will be in English, French, German, and Italian.

The Tables will contain all available information of value concerning the physical properties and numerical characteristics of (*a*) pure substances, (*b*) mixtures of definite composition, (*c*) the more important classes of industrial materials, (*d*) many natural materials and products, and (*e*) selected data for certain bodies or systems, such as the earth and its main physical subdivisions, the solar and stellar systems, and certain biological organisms, including man. Publications of the world in many languages have been combed for data and much unpublished information has been collected. The scope of the tables is so immense and of such an unprecedentedly comprehensive character, that special attention has had to be given to the arrangement so as to enable the Tables to be used with facility and dispatch.

For pure chemical substances the data will be assembled in tables of properties, but a certain amount of latitude and duplication will be permitted in some instances, and tables of materials will be employed where it proves to be more convenient.

In some cases no definite value of a constant can be put down, but only upper and lower limits. In other cases a graph may be the best means of indicating the variation of the particular property in question. Whatever method of presentation is employed it will be such as best to bring out the main purpose of the Tables, which is to take stock of our present quantitative knowledge of material things and to prepare in convenient form a critical digest of such knowledge.

The importance of securing uniformity in the case of fundamental constants, conversion factors, etc., has not been lost sight of, nor the importance of associating, where possible, with the data for a particular specimen or material, a statement of the exact experimental conditions, life history, etc.

The Tables will be issued in a series of volumes comprising a total of about 2500 pages ($9\frac{1}{2}$ in. × 7 in.), publication extending over about a year and a half. The progress made has been such that the first volume is now in the Press and may be expected during the early months of 1925.

The published price of the Tables will be from $60 to $75 for the set, but the Trustees are reserving the privilege of purchasing from the publishers at the rate of $35 per set whatever number of sets may be required to fill all advance subscriptions received by the National Research Council of America up to a definite fixed date, probably April 1st or May 1st, 1925, after which date the privilege will lapse, and subsequent sales will be handled exclusively by the publishers at the higher rate. $35 represents only the cost of printing, but the Trustees and the National Research Council are anxious that all scientific men and women shall be given the opportunity of taking advantage of the lower rate. Accordingly, arrangements are being made so that (1) members of a recognised scientific, technical or engineering society, or (2) Universities, research laboratories, libraries, government departments or the like, will shortly be given preferential facilities for purchasing sets at the lower figure before the expiration of the above-mentioned date. Only one such set may be subscribed for by one individual, but a reasonable number of sets may be purchased by organisations such as the above.

The National Research Council will deal with such applications, but all orders placed in the ordinary way through the Trade will be handled by the Publishers at the higher figure.

The Advisory Committee for the British Empire (excluding British North America) consists of Dr. G. W. C. Kaye (Corresponding Editor), Sir Robert Robertson, F.R.S., Dr. W. Rosenhain, F.R.S., Prof. A. W. Porter, F.R.S., Dr. T. E. Stanton, F.R.S., Mr. J. E. Sears (Jr.), Mr. A. C. G. Egerton, and Mr W. F. Higgins as Secretary. Dr. Rosenhain is also acting as Special Editor for Metals and Alloys. It is requested that any correspondence from the British Isles with reference to the Tables should be addressed to Dr. Kaye, The National Physical Laboratory, Teddington, Middlesex.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

Fig. 1 *a*.—HoL_{III}.

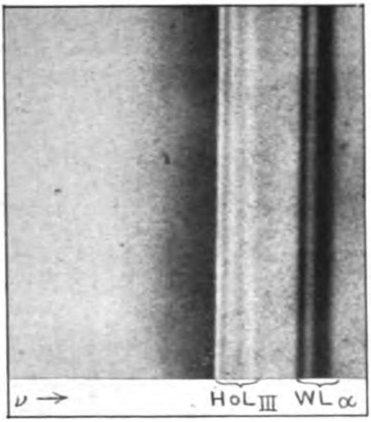
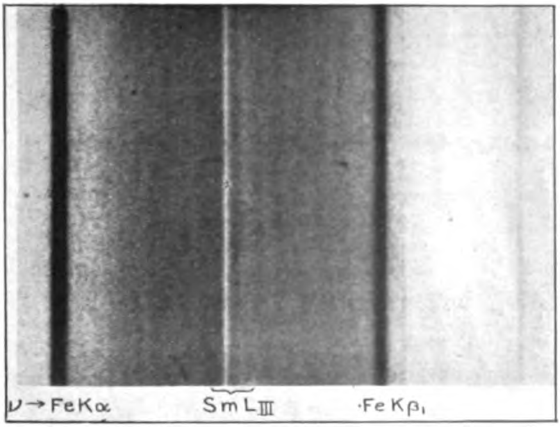


Fig. 2 *a*.—SmL_{III}.



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[SIXTH SERIES.]

APRIL 1925.

LXVIII. *The Electrical Behaviour of Radioactive Colloidal Particles of the Order of* 10^{-5} *cm. as observed separately in a Gas.* *By* FELIX EHRENHAFT, *Dr.Phil., Acting Professor of Physics and Head of Physics Institute III. of the University of Vienna* [*].

§ 1. UNTIL a few years ago all the observational data which we possessed were sufficiently explained by the Rutherford hypothesis—that the α-particles of radioactive substances all had identical charges and properties. Lately, again, Henderson [†], experimenting with α-particles which had passed through matter, deduced that they can carry double or single charges or be uncharged. I am interested, nevertheless, in those experiments of the Rutherford school where Kapitza [‡] has succeeded in photographing the tracks of α-particles under a strong magnetic field in a Wilson chamber. It was found that these tracks were of various kinds, having each its own curvature The writer had already pointed out, some years [§] ago, that all deductions concerning α-particles had to do with average values, and that we could not really speak of having determined the actual *individual* charges. This idea seems to have received definite support from Kapitza's experiments, for the experimenter himself treats the separate α-particle charges as a function of the distance travelled, and the reader of the article can see that the charge of one single α-particle, for example, varies from 2×10^{-10} to 7×10^{-10} e.s u.

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[*] Communicated by the Author.

[†] Proc. Roy. Soc. cii. p. 496 (1923).

[‡] Proc. Camb. Soc. xxi. p. 511 (1923).

[§] *Wiener Akad. Ber.* cxxiii. (ii. *a*) p. 61 (1914); *Ann. d. Phys.* xliv. p. 664 (1914); *cf.* also, *Wiener Akad. Ber.* cxix. (ii. *a*) p. 816 (1910).

This state of affairs induces me to draw attention to investigations which I have been carrying on for more than fifteen years and which may be of interest for their application, set out in detail below, to radioactivity and as bearing directly on these experiments of the Rutherford school.

§ 2. The charge on the electron enters as a fundamental physical constant into many theories of modern physics as well as into the science of radioactivity. As early as 1910 the writer had strongly emphasized the idea [*], that it was only by averaging the observations on groups of particles, or other averaging processes, that one could obtain the elementary indivisible quantum charge on the electron, as demanded by the fundamental hypothesis of the electron theory. The writer had himself observed the motions of small spherical particles of silver, of the order of 10^{-5} cm., in a gas, and, by averaging, had deduced [†] a charge for these particles of the order of the so-called elementary quantum. It was clear, however, that such a procedure, where average values are depended upon, is incomplete. For this reason, even before the publication of these results, the writer had given a method [‡] (*Anzeiger d. Wiener Akad. d. Wiss.* no. vii.

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[*] Vide *loc. cit.*

[†] *Wiener Akad. Ber.* cxviii. (ii. *a*) p. 321 (1909).

[‡] Since Prof. Millikan has opened up, in several English publications, the question of priority in the method of determining electric charge on individual particles, and since, by reason of the war, I could only reply in German ones (*Ann. d. Phys.* lvi. p. 58, 1918), I should like to be allowed to make the following remarks:—

Prof. Millikan has changed his standpoint on the priority question, for, at first, he wrote in the Phys. Rev. xxxii. p. 392, April 1911: "The only other investigations which appear to yield results which are in any way adverse to the conclusions herein contained are reported in very recent papers of Ehrenhaft and Przibram, both of which have appeared since this work was first presented to the Physical Society on April 23, 1910." His contention was thus, all this time, limited to independence in discovery of the method. On the other hand, he wrote later on, in the Phys. Rev. viii. (n. s.) p. 596, Dec. 1916, as follows: "Ehrenhaft, in a paper read at the Naturforscherssammlung zu Königsberg in Sept., 1910, made a very clear statement of this defect in his own attempted determination of *e*, and asserted that it inhered also in the work of all other observers. *As a matter of fact, however, I had the good fortune to find a way of removing this limitation entirely more than a year earlier, viz., in the spring and summer of 1909.*" He is here already claiming priority and in fact modifying the standpoint he had taken up to this time, as is shown by his article in Phil. Mag. xix. p. 209, Feb. 1910, concerning which we shall have something to say below. In 1917 he goes so far, indeed, as to write in Phil. Mag. xxxiv. p. 1, July 1917: "For, first, Professor Ehrenhaft and his pupils began publishing in 1914 a

March 4, 1909 ; no. x. April 21, 1910 ; no. xiii. May 12, 1910) enabling us to determine the charge on the smallest possible

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series of results which, though obtained by a modification of my method, were wholly irreconcilable with the results which I had found." That is, he now dates the beginning of my writing about five years too late, a presumption which cannot be entertained.

The actual state of affairs is, however, as follows: As early as the no. 7 issue, March 4, 1909, of the *Anzeiger der Wiener Akad. d. Wiss., i. e.* before the publication by any other writer on this point, I expressly pointed out that the measurement of the electric charge on *single particles* supplied a new method for the determination of the elementary electric quantum. Also in an exhaustive article of March 18, 1909, in *Sitzungsber. d. Wiener Akad.* cxviii. (ii. *a*) p. 321 and in the *Phys. Zt.* x. pp. 308–310, I established the fact that the method I had developed for measuring charges could be applied to individual particles and would enable us to calculate the charge of a single particle. Millikan, on the other hand, has not pointed out the *necessity* for measurements by the aid of single particles either in his preliminary communication of Dec. 1909 (Phys. Rev. xxix. p. 260) or in his more complete paper on cloud particles, Phil. Mag. xix. p. 208, Feb. 1910. Neither is this to be wondered at, for, as can be clearly seen from the last named article, he arrived only accidentally at the method of observations on single particles. (In this connexion, *cf.* lines 20 to 32, p. 216, of the article in question.) Accordingly he does not apply his readings to these particles separately—a point I have already made in the *Wiener Akad. Sitzungsb.* cxix. (ii. *a*) p. 825 (1910), and in the *Phys. Zt.* xi. p. 942 (1910)—but takes their mean. It was I who first recalculated Millikan's results for separate particles and could thus demonstrate, for example, that in a group to which he accorded 3 quanta he had averaged a water particle which by my calculation carried $15{\cdot}59 \times 10^{-10}$ e.s.u. Another water particle for which I calculated the separate charge of $15{\cdot}3 \times 10^{-10}$ e.s.u. was included in a group in which was given 4 quanta. It follows that my papers, which appeared in the Academy *Anzeiger* no. 7, March 4, 1909, no. 10, April 21, 1910, and no. 13, May 12, 1910; in the exhaustive article in the *Sitzungsber. d. Wiener Akad. d. Wiss.* May 12, 1910, and also the paper read at the Science Meeting at Königsberg (*Phys. Zt.* xi. pp. 940–949, 1910), are the first ones dealing with the charge on individual particles which discuss the question of the existence or non-existence of an electron. They are also the first in which observations were taken and calculations made on separate particles. On the other hand, Millikan's first papers in which he recorded and calculated from separate particles appeared first in Dec. 1910 in the *Phys. Zt.*, the first in English being in the Phys. Rev. of 1911. He, therefore, did not abandon the Wilson cloud method to adopt the method of observation and calculation with separate oil drops until Dec. 1910 in the *Phys. Zt.*

It is clear from this that the point of view that the existence of an elementary quantum was to be proved by measurements on individual particles was brought forward and carried out in the first place by the writer, whereas Prof. Millikan had up till then employed only charge averages, and this is of course quite easy to understand, for he had never had any doubt concerning the existence of an elementary quantum of electricity.

particle in a gas. This method was next treated exhaustively in several papers [*], and again the point was discussed at large at the Science Meeting in Königsberg [†]. The fundamental idea in all this was that we can *most probably expect to find the smallest electric charge on particles of the smallest capacity.* These test bodies of smallest capacity must, however, be still large enough to be optically and separately perceived and subjected to physical measurement. We are therefore directed *à priori* to particles whose dimensions correspond with the limiting powers of the microscope. Test bodies of the noble metals or mercury have the special properties of great density and reflecting power which allows them to be individually seen against a dark background down to sizes where other particles are invisible. Moreover, spheres of the noble metals are definitely determined chemically and have, as inert substances, great stability in the inert gases. I have further convinced myself of the sphericity of the test bodies which I used for this purpose. They displayed symmetry against a dark background from all directions and suffered no orientation in an electric field. Furthermore, precipitations of such particles, when resolved with large-aperture microscopes, showed exact sphericity [‡].

Let us consider, say, a mercury sphere of the order of 10^{-5} cm. in an inert gas, nitrogen or argon, and observe it in the gas space between two horizontal metal plates. Let the plates have a diameter of 8 to 9 mm. and be 1 to 2 mm. apart. By suitable arrangements this small space is completely isolated from other gas. Between the plates apply a variable vertical electric field E. The space between the plates is illuminated by the diffuse portion of a beam of light emitted by a horizontally adjusted microscope objective. The observing microscope is adjusted at right angles to this beam. It is then an easy matter to observe against the dark background the uniform speed of this brilliant mercury sphere under the influence of an external force P. In particular, if the test body carries a constant charge e and the field strength in the condenser is E, then the force acting vertically upwards on the body is $eE-mg$, where

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[*] *Wiener Akad. Ber.* cxix. (ii. *a*) pp. 815–866 (May 1910); *Phys. Zt.* xi. pp. 619–630 (1910).

[†] *Phys. Zt.* xi. pp. 940–949 (1910).

[‡] *Cf.* the tables in the *Wiener Akad. Ber.* cxxiii. (ii. *a*) p. 53 (1914); *Ann. d. Phys.* xliv. p. 664 (1914); *C. R.* clviii. p. 1071 (1914); *Phys. Zt.* xvi. p. 227 (1915); *ibid.* xviii. p. 352 (1917); *Ann. d. Phys.* lvi. pp. 1, 81 (1918); *ibid.* lxiii. p. 773 (1920). For further proofs of sphericity, *cf.* also *Ann. d. Phys.* lvi. p. 54 (1918).

mg is the weight of the mercury particle. It is the limiting steady velocity of such test bodies, attained under the influence of constant external forces in a resisting medium, which we are required to measure as *base* for conclusions. The speed of the test body is proportional to the force acting on it, and hence, in particular, if the force $eE-mg$ acts vertically upwards the velocity is $(eE-mg)B$, where B is the mobility, *i.e.* the speed attained by the body under unit force. The observed speed must, therefore, vary linearly with the field strength if the mobility is actually a constant, and this can, in fact, be demonstrated over wide ranges [*].

It remains to define the mobility constant, B, for the test body, and in defining it we also give its magnitude. For this purpose the writer has, up to the present, employed four methods:—

(1) The hydrodynamical method of determining the mobility from the Stokes law of fall for spheres in resisting gaseous media. This is the classical method by which J. J. Thomson and his school determined the size of a falling "cloud" particle. At the Science Meeting in Königsberg (1910) I drew attention [†] to the fact that in this case Cunningham's correction has to be applied [‡].

(2) An optical determination [§] of the magnitude of the particle and with it the mobility. To this end the writer observed the colour of the light scattered. For these bodies are small enough for individual selective colouring to be visible in the microscope: in general, the smaller the sphere the shorter is the wave-length of the perpendicularly diffracted light, though the colour of this diffracted light depends also upon the optical constants of the sphere. If, therefore, we calculate the colour of the light radiated from a sphere of known size, we can deduce the size of the test body from its observed colour.

(3) The writer could also determine the size and mobility from the photophoretic maximum [||] of the forces acting on a silver particle. We assume in this that the positive photophoretic force of light on silver is identical with the light pressure. I have already shown [¶] that small test bodies in

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[*] *Ann. d. Phys.* lxiii. p. 782 (1920).

[†] *Phys. Zt.* xi. p. 952 (1910); *Wiener Akad. Ber.* cxix. (ii. *a*) p. 860 (1910).

[‡] See Fritz Zerner, *Phys. Zt.* xx. p. 546 (1919).

[§] F. Ehrenhaft, *Phys. Zt.* xv. p. 952 (1914); xvi. p. 227 (1915), etc.

[||] *Phys. Zt.* xviii. p. 367 (1917).

[¶] F. Ehrenhaft, *Ann. d. Phys.* lvi. p. 81 (1918): "Die Photophorese."

gases are driven either with the light, "light-positive," or against it, "light-negative." The discussion of the nature of these forces is by no means at an end. Assuming, however, that the light-positive action on silver, which has a high reflective power, arises from light pressure; since light pressure for certain spheres must be specially strong [*], we can draw conclusions regarding the size of these spheres from observations of the maximum action.

(4) Finally, the mobility [†] can also be deduced from the Einstein theory [‡] of the Brownian movement in gases [§]. This method seems to the writer, however, the most untrustworthy of all inasmuch as it gives results differing [‖] from those of the other three, while the latter are self-consistent.

From the very first I found charges on individual test bodies, from metals as well as from mercury, which were often only small fractions of the so-called elementary quantum of electricity. The general conclusion was reached that test bodies below a radius of 3×10^{-5} cm. often carry charges smaller than that of the electron and, hence, that the charge on test bodies decreases [¶] on the average with their capacity (and hence radius). In this connexion charges of the order of a tenth or twentieth part of the electron's are by no means the smallest.

The most serious objection raised against this result, which contradicts the prevailing theory, has been that the test bodies which I used were not spheres; but this is, of course, sufficiently met by microphotographs and direct observation, if, indeed, one is inclined at all to doubt determined sphericity in the case of minute mercury particles [**].

A further objection has been that the density of the test body was not that of the molar (bulk) substance. Under the high-power microscope, however, the spheres still show the colour and glitter of the molar substance. Nevertheless, the quite implausible assumption has been made that the density of platinum (21·4) or mercury (13·56) could vary from particle to particle and in the case of platinum, for example, sink[*] to 0·2. Such assumptions are actually necessary if the charge $4{\cdot}774 \pm 0{\cdot}004 \times 10^{-10}$ e.s.u. is to be accorded to individual test bodies.

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[*] See P. Debye, *Ann. d. Phys.* xxx. p. 57 (1909).

[†] E. Weiss, *Wiener Akad. Ber.* cxx. (ii. *a*) p. 1021 (1911); F. Ehrenhaft, *Verh. d. deutsch. phys. Ges.* xv. p. 1187 (1913), etc.

[‡] A. Einstein, *Ann. d. Phys.* xvii. p. 549 (1905); xix. p. 371 (1906).

[§] F. Ehrenhaft, *Wiener Akad. Ber.* cxvi. (ii. a) p. 1175 (1907).

[‖] Cf. *Ann. d. Phys.* lvi. p. 71 (1918); S. Landman, *Zt. f. Physik*, xxvii. p. 237 (1924).

[¶] Cf. *Phys. Zt.* xii. p. 103 (1911).

[**] M. A. Schirmann has recently in my department (*Phys. Zt.* xxiii. p. 441, 1922) investigated light polarized by diffraction from submicroscopic particles of Hg, Au, Cu, Pb, oil, and a modification each of S, Se, and Te, which were still smaller than the above test bodies, and has shown their complete symmetry for all orientations.

As a third objection it has been maintained that the test bodies are surrounded by gas layers[†] resulting in the deduction of wrong charges. This hypothesis also seems untenable, for with modern methods of investigation in this region, carried out, it is granted, on matter in bulk, the contrary conclusion was reached, viz. that no gas layers are found to any extent that matters. At the most we find layers of the order of one molecule[‡] thick. It is, further, impossible to imagine what forces could cause gas layers great enough to influence the results.

Finally, it has often been emphasized that the exact form of the law of resistance for such small spheres in a gas (*e. g.* Stokes, Stokes-Cunningham, Knudsen-Weber, Millikan, Zerner, Lenard, Epstein) is not yet known. We must, of course, keep in mind that if, on the one hand, the validity of the resistance law for small moving spheres of mercury and other material is to be doubted, then it cannot hold, either, for other substances, *e. g.* oil. The withdrawal of such a premiss would of course cut the ground away from the elementary quantum idea of $4{\cdot}774 \pm 0{\cdot}004 \times 10^{-10}$ e.s.u. as deduced from observations of electric charges on individual oil drops on the assumption of the validity of one of these laws. The writer, however, has all along taken the stand that an exact and purely empirical derivation of the resistance law for small spheres falling in a gas, which has hitherto been only theoretically formulated or found by observations on large spheres, is still to be attained. At the same time, we must take care that the experimental derivation of this resistance law does not contain the presupposition of an indivisible electron, as has been done in the well known work of R. A. Millikan. Such a procedure is a case of *petitio principii*. No significance can therefore be attached to resistance laws derived in this manner from which in turn the electronic charge is deduced, its existence, of course, being by such methods easily demonstrable. The exact determination of a resistance law must follow from a method which is completely free from any assumption of the existence or non-existence of an elementary quantum, as well as of the divisibility or indivisibility and also of the equality of charge on the various drops. Such an investigation has long been going on in this Institute and is nearly completed. The purely mechanical and experimental determination of the correction to be applied to Stokes' law for the motion of a small sphere in a gas has thus not as yet been realized. It is, however, to be remarked that the final result of the experiments which are discussed below is independent of the exact numerical value of the quantity *

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[*] R. Bär, *Ann. d. Phys.* lxvii. p. 193 (1922). Against this, *cf.* Th. Sexl, *Wiener Akad. Ber.* cxxxii. (ii. *a*) p. 139 (1923); *Zt. f. Physik,* xvi. p. 34 (1923); *Zt. f. Physik,* xxvi. p. 371 (1924).

[†] *Cf.* my remarks in the discussion at the Science Meeting in Nauheim, *Phys. Zt.* xxi. p. 624 (1920).

[‡] *Cf., e. g.,* I. Langmuir, Journ. Amer. Chem. Soc. xl. p. 1361 (1918); F. Paneth, *Zt. f. phys. Chemie,* ci. pp. 445, 480 (1922); *Zt. f. Electrochemie,* xxviii. p. 113 (1922); *Zt. f. angew. Chemie,* xxxv. p. 549 (1922).

$$B = \left[1 + \frac{l}{a}\left(A + De^{-C\frac{a}{l}}\right)\right] \Big/ 6\pi\mu a.$$

On the other hand, it is important to demonstrate for later deductions that the electric field is of uniform strength and direction at all points between the plates of the condenser. An ideal *ballon-sonde* for investigating the field is a test body of the order of 3×10^{-5} cm., say a mercury sphere of constant charge, for it is infinitely small as compared with the length of path observed and the condenser dimensions. It turns out that this test body is driven with constant speed † and direction in all parts of the field. Whence it follows that the field is completely constant at all points of the condenser, and the *proviso* of a homogeneous field is satisfied.

Such a colloidal test body with constant charge may even be used as an electrometer, for it is easily found that it rises with uniform speed in a field of constant gradient. If, however, we suddenly cut off the voltage from the condenser plates the upward motion becomes less and less, the body finally stops, turns about, and begins to fall with acceleration. This procedure can be repeated indefinitely on the same test body, and the reason for the phenomenon is quite clear. When the plate tension is cut off the condenser charge passes through the ebonite insulation of the container and is dissipated outside. In this way the potential difference varies and with it the field between the plates. The magnitude of the field is given at every instant by the speed of the test body. The electric force acting on it is at first still greater than its weight and so it rises with continuously decreasing velocity. These forces ultimately become equal and the body halts. Then the electric force is exceeded by gravity and the body falls with increasing speed. We thus see that in such experiments the test body assumes the function of an electrometer, for it enables us to calculate easily the tension on the condenser plates from the velocity observed.

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* l, mean free path of the gas molecule.
μ, coefficient of internal friction for gases.
a, radius of test body.
A, D, C, constants.

† *Cf.* F. Ehrenhaft and D. K. Konstantinowsky, "Radioaktivität und Elektrizität," *Ann. d. Phys.* lxiii. p. 780 (1923).

It can thus be seen from these details that such a colloidal particle makes an ideal instrument for determining the quality and direction of the field, and, finally, that knowing the capacity * of the condenser in which it serves as electrometer, information is given as to the condenser's rate of leak.

A test body possesses, in general, a mean constant rate of rise or fall in a field of constant strength, and from this we deduce that it also possesses constant mass and charge. If we vary the charge on the test body at any time, it is well to remove the electric field for an instant and at the same time ionize the gas between the condenser plates by outside means (radium preparations, Röntgen rays, ultraviolet light, etc.). On reapplying the field the motion of the same test body is again observed. It is then often found that a new velocity, in the same or the opposite direction, has been acquired, so that a variation of charge on the test body is deduced from the change in velocity. The charge on the particle is then said to have been varied from outside.

§ 3. In 1909 I set myself the problem of measuring the electric charge on the smallest possible individual particles and thereby subjected the foundations of the electron theory to a sharper test. Similarly the present problem is to follow, if possible, radioactive phenomena not statistically, as done hitherto, but observing the detail of the time variation of the radioactive process itself. I have succeeded † in doing this by investigating the motion of a small colloidal spherical

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[*] Cf. *Ann. d. Phys.* lxiii. p. 792 (1920).

[†] These and the following investigations were carried out with Dr. D. Konstantinowsky, who was my assistant at that time.

test body, which was radioactive and of dimensions of the order of 10^{-5} cm., in a constant electric field.

The first thing to do was, thus, to transform small test bodies of these dimensions into a radioactive condition. As is well known, the writer has been able to form spherical particles of any substance, *e. g.* mercury or selenium, by vaporization. Radioactive particles can also be formed in this manner. For this purpose, radium emanation was enclosed in a vessel with selenium powder or mercury and the vessel was shaken for several hours, so that the breakdown products of the radium emanation—radium A to radium D—were shaken out upon the substance used. The excess emanation was removed and the infected substance brought into another chamber (a small bulb) *. To remove all remains of the emanation that might have been occluded, the bulb and contents were heated and at the same time dry pure gas allowed to pass through it. Such test bodies must necessarily emit radiations of all kinds (α, β, γ, δ) on account of the radioactive substances produced. To obtain, further, a radiation of α rays only, we separated out electrolytically polonium on selenium. The selenium was actually found to be a radiator of α rays only.

It is now possible by suitable arrangements † to bring a single one of these test bodies between the plates of my condenser and subject it at once to measurement. The very first one showed a quite different behaviour from that of the non-radioactive particles. The movement in the constant electric field was no longer uniform, and the particle often changed from one type of motion to another with accompanying change of speed, giving one completely the impression of a continuous change of electric charge.

We must therefore next follow the phenomenon quantitatively by registering the velocity of the test body as nearly continuously as possible. The times required by the falling particle to pass successive scale-divisions of the observing microscope were recorded. The field was then so altered that the same particle rose past the same divisions, at the same point in the condenser. The change of field in the condenser was brought about in such a way as always to have a voltage difference on the plates. The test body was thus at no time in a field of no gradient. The following figures give some idea of what happens :—

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* Cf. *Ann. d. Phys.* (4) lxiii. p. 813 (1920).

† Cf. *loc. cit.* p. 787.

Fig. 1.

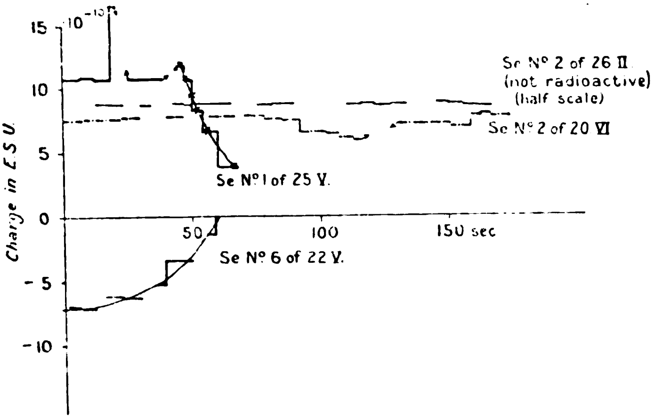


Fig. 2.

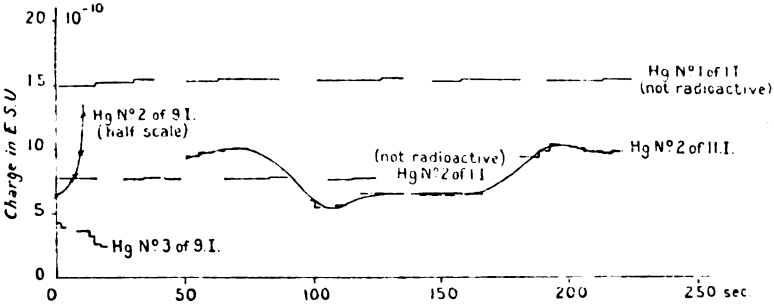


Fig. 3.

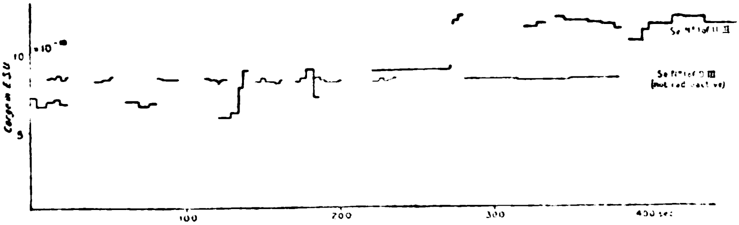


Fig. 4.

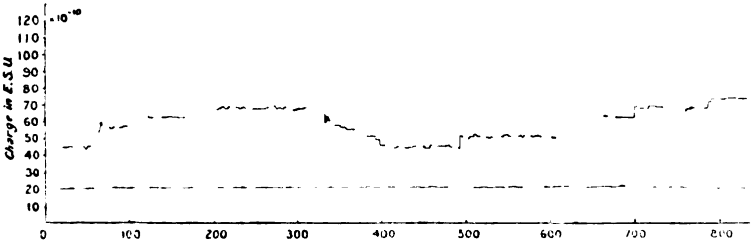


Fig. 4 *a*.

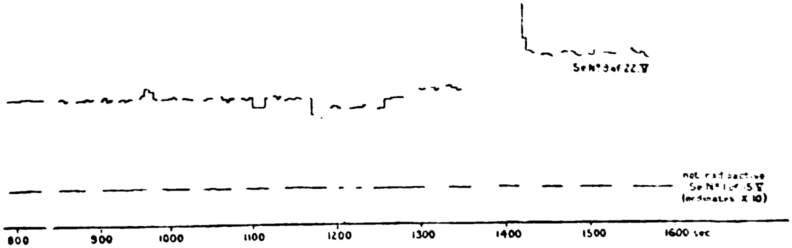


Fig. 5.

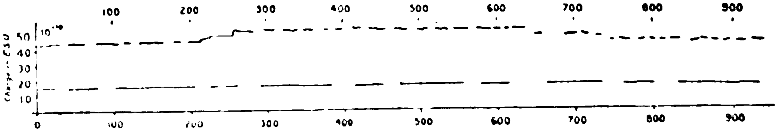
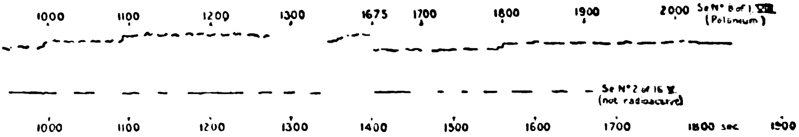


Fig. 5 *a*.



In the above figures the average charges are plotted as ordinates against the times as abscissæ; the individual points corresponding to continuously varying charges cannot be determined, but only the average values of the charges during the periods of rise or fall while the test body passes a few successive divisions of the eyepiece scale. Non-radioactive test bodies were introduced as a check, and fit extraordinarily well along a straight line parallel to the abscissa axis. The minute variations of these step curves are sufficiently accounted for by observational errors. The charges on the test bodies sometimes vary extraordinarily—sometimes in shorter, sometimes in longer periods. For example, the selenium particle no. 1 of May 20 (fig. 1) after about 20 seconds shows an apparent abrupt variation in charge of about 6×10^{-10} e.s.u., followed immediately by a return to the original positive charge of a little over 10×10^{-10} e.s.u. It retained this charge for about 20 secs., gained a small amount during the next half-minute, and then lost it gradually down to about 3×10^{-10} e.s.u. Readings were taken five times during this latter loss of charge. A second particle (selenium no. 6, May 22, fig. 1) lost its charge of about -7×10^{-10} e.s.u. in a minute, and so on. It, too, was recorded five times. The particle mercury no. 2 of Jan. 9 (fig. 2) varied in charge continuously over some ten seconds from about 13×10^{-10} e.s.u. to, say, 25×10^{-10} e.s.u., and was recorded five times during this continuous increase. The charge on the particle mercury no. 2, Jan. 11, varied continuously between about 10 and 5×10^{-10} e.s.u. We must keep in mind, here, that these test bodies had been in contact with emanation and would therefore emit all four radiations α, β, γ, δ. A similar condition of affairs (*vide* figs. 3, 4, 4 *a*) is furnished by the particles, selenium no. 1 of Mar. 11, and selenium no. 9, May 22. The latter was under observation for 1600 secs. These variations should be compared with those under similar conditions and shown in the same figures, but given by the non-radioactive particles selenium no. 1 May 15, and selenium no. 1 March 9. On the other hand, the particle selenium no 3 Aug. 1 (figs. 5, 5 *a*) contained only polonium. It was observed over 2000 secs., showing seven slow continuous changes in charge and only one more rapid change. It could only be expected to emit α-particles. It is to be noted, in particular, that a series of test bodies observed over relatively long periods of 10 to 50 secs. showed an apparently continuous loss of charge, *e. g.* from 10 to 5×10^{-10} e.s.u. and from -7×10^{-10} e.s.u. to zero.

It might be objected here that the absolute charge on these test bodies is still somewhat indeterminate, since the question of determining the body's size from its velocity under gravity is not yet finally cleared up. For, as mentioned at the beginning, the purely mechanical determination of the correction term in the resistance law for small spheres falling in a gas is still to come. From the previous discussion, however, it is clear that the question turned rather on the exact determination of a small correction term. As regards deductions from these experiments such a question is of no importance, for when a particle loses its charge continuously in about 60 secs. from -7×10^{-10} e.s.u. to zero and is meantime eight times observed, it is all the same whether the absolute value of the charge at the beginning of the run was -7 or -6 or -8×10^{-10} e.s.u.

We must now ask whether these new phenomena can be explained without either having to make the assumption of charges smaller than those of the electron or subscribing again to the old idea of continuity in electricity. We calculated, for example, the impulse which would be given to the test particle by the ions imagined to have been generated by the impact of an α-particle and accelerated by the field, but it was found to be 10^6 times too small * to be at all observable. Static space charges cannot exist between the condenser plates, as there is always a high gradient (1 to 4 e.s.u. cm.), and it is only the test body which remains, owing to the suitable field regulation.

From this discussion it follows that the phenomenon of continuous charge variation on radioactive test bodies cannot, in my view at least, be regarded otherwise than as due to the fact that such small particles are capable of picking up or losing charges which are only quite small fractions of the supposed indivisible electronic charge. This is in agreement with the point of view I have represented for 16 years, that minute test bodies are frequently observed with charges which are to a different order of magnitude smaller than the electric charge.

The above results seem similar to those of Kapitza mentioned at the beginning, but it must be borne in mind that they were observed in a field of high potential gradient, so that they can no longer be explained by capture and loss of free electrons in the gas.

During the last three decades a series of phenomena have been observed in Physics which lead ultimately to the decision that the indivisible atom has to be broken up into smaller parts. What was considered indivisible up to a certain point, in time falls a victim at last to division. The case seems quite the same with the electron. There may be a group of phenomena capable of seeming explanation on the assumption of preferential charges. On the other hand, it does not seem justifiable under any circumstances to conclude that only certain preferred charges occur, *i. e.* are universal, all other conditions of charge being excluded. It is especially not clear why observations on individual charges should not show smaller charges, nor why the separate electrons cannot also be split up in the midst of such mighty energy changes as accompany radioactivity. And this is all the more true, since, as far as the writer is aware, there is up till now no theory of any kind to account for the electron's cohesion. A number of well-known investigators, such as Poincaré, Weyl, Einstein, etc., have raised the question of the electron's stability. No conclusion has been reached. This very question, however, implicitly contains the possibility of a break up. The point of view that the electron is in all cases strictly indivisible would place the question as to its stability among the superfluous. No investigator has so far, however, as far as I know, taken this stand.

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* Cf. *loc. cit.* p. 790.

I have to thank Mr. Herbert Bell, of Manchester University, for his great kindness and trouble in translating this article from German into English.

The University of Vienna,
December 1923.

APPENDIX.

An important advancement toward the purely experimental determination of a law of resistance in the sense indicated above, without the presupposition of the electron, has since been made in my department through the work of J. Mattauch, *Phys. Zt.* 1924. From observations of the same test-body under different gas-pressures, he succeeded in establishing a law of resistance, or in confirming the Knudsen-Weber law. I cite this although, as already mentioned, this circumstance is irrelevant as regards the conclusions of this paper. Further, important points concerning the nature of the different test-bodies might be obtained from the photoelectric properties of those individual test-bodies which, on illumination with ultraviolet light, very frequently give off positive charges (and indeed by fractions of the electron) and not exclusively negative ones as one might expect from the theory. (*Cf.* M. Hake, *Zt. f. Phys.* xv, p. 110, 1923, and E. Wasser, *Zt. f. Phys.* xxvii. p. 203, 1924.) However, departures from the elementary quantum must also have been observed in the researches of the Millikan school, for Ishida writes (Phys. Rev. xxi. p. 550, 1923): "There were a few cases that had to be discarded, the results being for some unexplained reasons 10 to 50 per cent. out." Silvey likewise communicates (Phys. Rev. vii. p. 87, 1916): "As a rule, however, the more slowly falling particles indicating no evaporation, gave values for the ultimate charge much lower than if they had been pure mercury droplets with the same speed under gravity, although the change in charge was an exact multiple of the charge originally on the droplet." As is known, Millikan uses the mercury droplets observed by Derieux besides oil as a second experimental material for the determination of the electron. Th. Sexl (*Zt. f. Phys.* xxvi. p. 371, 1924) has shown that these give results departing from the elementary quantum provided one computes with the law of resistance consistent with the mechanical conditions (*i. e.* determined by the velocity of fall of the same test-body under different gas-pressures). *The discrepancy appears to lie, therefore, not at* *all in the observations but in the interpretation of the experimental results.*

The University of Vienna,
December 6th, 1924.

[Since the war period inevitably perturbed the inter-relations between Austrian and American science, it seems fair to allow space for Professor Ehrenhaft's contention about the fundamental unit of electric charge, which he regards as not an indivisible unit. But it is also fair to Professor Millikan to point out that in his book, 'The Electron,' published in 1917, he devoted a long chapter to a discussion, and what he considered a refutation, of Professor Ehrenhaft's contention that the existence of fractions of an electronic charge were demonstrable:

(1) by criticism of statistical methods,
(2) by the Brownian movement,
(3) by direct observation of microscopic silver particles in a horizontal electric field.

Professor Millikan's own words, near the end of Chapter VIII., are as follows:—

> "While then it would not be in keeping with the spirit or with the method of modern science to make any dogmatic assertion about the existence or non-existence of a sub-electron, it can be asserted with entire confidence that there is not in Ehrenhaft's experiments a scrap of evidence for the existence of charges smaller than the electron. If all of his assumptions as to the nature of his particles are correct, then his experiments mean simply that Einstein's Brownian-movement equation is not of universal validity, and that the law of motion of minute charged particles is quite different from that which he has assumed. It is very unlikely that either of these results can be drawn from his experiments, for . . . . [certain verifications of the law have been given] . . . . . I have thus far found no evidence of a law of motion essentially different from that which I published in 1913.
>
> "There has then appeared up to the present time no evidence whatever of the existence of a sub-electron."

The last sentence is printed by Prof. Millikan in italics.

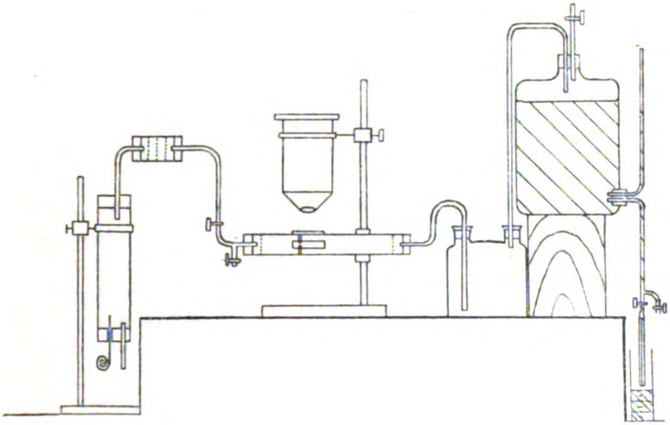
Nevertheless the fundamental importance of the atomic nature of electricity, and the size of its ultimate unit, is so great that no serious attack on the orthodox position can be ignored. O. J. L.]

LXIX. *On Eddies formed behind Apertures through which Air is Streaming.* *By* A. L. GRIFFITH, *B.Sc.*, *and* ALFRED W. PORTER, *D.Sc.*, *F.R.S.* *

THE work described in this paper is complementary to that on "Eddies in Air" (Phil. Mag. xlvi. p. 754) by Nisi and Porter, since it deals with apertures in plates instead of obstacles.

The flow of gas took place in a cylindrical metal chamber, of square section, divided by a transverse metal frame in which the plates containing the apertures were successively fitted. The complete apparatus is sketched in fig. 1.

Fig. 1.



Arrangement of Apparatus and Experimental Description.

Water flows from a ten-litre aspirator and causes a suction which draws air through the whole apparatus. The air first enters a large chamber in which smoke is produced. This smoke is picked up by the air, and carried along through a smaller chamber containing three gauze obstacles which stop the heavier and larger smoke particles and steady the general flow. The smoke-laden air now passes into the observation chamber. This consists of a square-section brass tube containing at each end a fine gauze to steady the flow, and, one-third along its length, a diaphragm in the middle of which is the aperture to be experimented with.

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* Communicated by the Authors.

Two sizes of observation chamber were used—the smaller $2{\cdot}6 \times 2{\cdot}6 \times 30$ cm. and the larger $5 \times 5 \times 30$ cm., with aperture varying from ·25 cm. to ·05 cm.

In the middle of the observation chamber, windows were cut in the sides and top, and these were covered with thin glass plates. Horizontal illumination was provided by a 5–10-amp. carbon arc, the light from which was focussed by suitable lenses into a thin horizontal sheet in the axial plane of the chamber in the neighbourhood of the diaphragm, heat-filters being employed to reduce the heating effect of the arc to a minimum. After passing through the observation chamber, the air traverses a five-litre vessel which minimizes any tendencies towards pulsations in the gas-flow. Thence it passes to the aspirator.

The phenomena were observed vertically by the light scattered by the smoke particles being focussed by a camera lens of wide angle and short focal length. The image of the smoke was focussed on a graduated ground-glass screen which, if necessary, was replaced by a photographic plate, and a photograph taken.

At first, horizontal flow and horizontal observation were used, but the latter had to be abandoned because the gravity effect on the smoke cloud produced dissymmetry in the field of view. The lower part of the field contained the larger particles, which had settled owing to gravitation, and the photographic exposure necessary for these was very different from that required by the upper part.

Various kinds of smoke were tried (*e.g.*, tobacco smoke, powdered silica, ammonium chloride, and magnesium oxide), but magnesium oxide was used for most of the observations. Typical cases were photographed, but in the majority of cases eye observations only were taken.

The flow of water from the aspirator was controlled by a system of capillary tubes, and the mean velocity of the gas in the aperture was calculated from the rate of flow of water from the aspirator. This rate of flow was measured by means of a graduated tube and a stop-watch.

The room temperature was noted each day of experiment, and it was found that the slight daily variations of temperature had an inappreciable effect on the experiments.

Notation.

Throughout this paper the following notation is used :—

d, diameter of aperture.
D, diameter of observation chamber.
Z, longitudinal distance from diaphragm.
X, transverse distance from axis of chamber.
y, mean velocity of gas in aperture.
y_c, mean critical velocity of gas in aperture.
v, longitudinal velocity of gas in chamber.
w, transverse velocity of gas in chamber.

PART I.

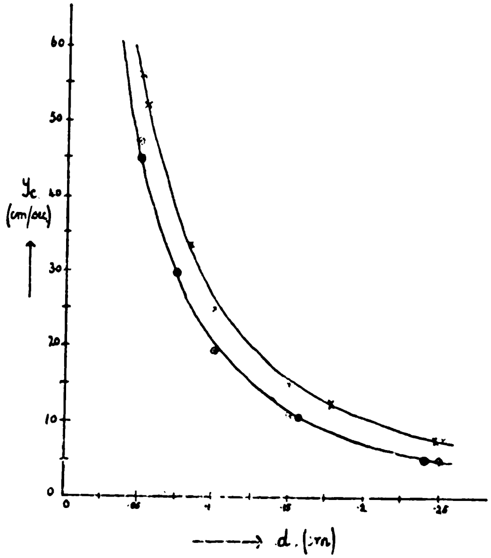
The Relation between the Dimensions of the Apertures and the Critical Velocities.

It was found on first using the apparatus described, that on varying the gas velocity three distinct types of motion occurred. First of all a steady stream-line flow of the gas through the aperture is seen ; then, as the velocity increases this stream-line flow ceases, and a steady eddy motion takes place, the centres of the eddies formed having fixed positions in the chamber. Lastly, as the velocity is increased still further, the eddies are no longer stationary, but move down the tube as soon as they are formed.

The critical velocities studied were (1) those between stream-line flow and steady eddy motion, and (2) those between steady eddy motion and unsteady eddy motion. Each aperture is in reality a short tube of length equal to the thickness of the plate. Four such cylindrical tubes were used successively in each chamber. The diameter of these apertures ranged from ·05 to ·25 cm. Each critical velocity was measured both when the velocity was being increased and when it was being diminished. This was repeated several times, so that each critical velocity was determined six to ten times. The temperature of the air-stream was noted in each case, magnesium oxide being the smoke used. In all this work it was found necessary to use a somewhat long heat-filter and a small light stop, in order to render the heating effect negligible.

The critical velocities determined from observations of the moving particles were plotted as graphs against the diameters of the apertures (figs. 2 and 3).

Fig. 2.



Critical Velocity between Stream-line Flow and Steady Eddy Motion.

× Large Chamber. Experimental Points.
⁘ do. Points from Formula.
⊙ Small Chamber. Experimental Points.
◌ do. Points from Formula.

Each critical velocity gave one curve for each tube, all of the same general shape, the pairs of curves for the two types of critical velocity being of somewhat similar shape, although we have not found it possible to represent both by similar algebraic equations.

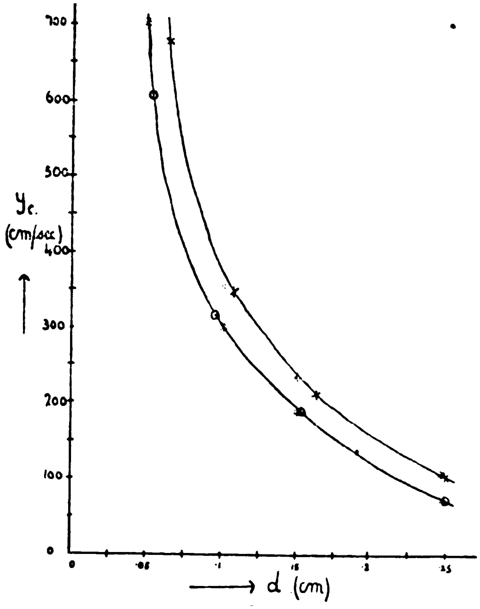
Various types of equations were tried for these curves, but the best results were obtained using an equation of the general form

$$y_c = \mathrm{A}\frac{\mu}{\rho d}\left[1+\mathrm{B}\left(\frac{d}{\mathrm{D}}\right)\right]^n,$$

which is dimensionally correct if A and B are numerics.

In the case of critical velocity between stream-line motion and steady eddy motion A = 20·1, B = 12, and $n = -1$, while

Fig. 3.



Critical Velocity between Steady Eddy Motion and Unsteady Eddy Motion.

× Large Chamber. Experimental Points.
⁘ do. Points from Formula.
⊙ Small Chamber. Experimental Points.
◌ do. Points from Formula.

for that between steady eddy motion and unsteady eddy motion $A=270$, $B=-4·2$, and $n=3/2$. It must be clearly understood that such a formula as the above can only hold for small values of d/D.

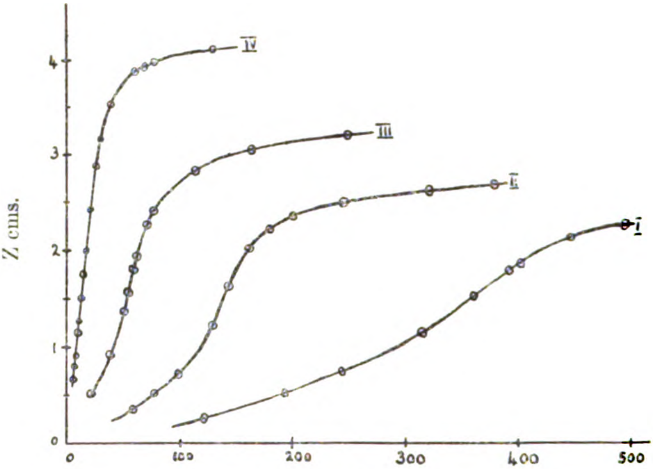
PART II.

The Distances of Eddy Centres from the Plane of the Aperture.

The same four cylindrical tubular orifices were used in each chamber, and the longitudinal distances of the eddy centres from the diaphragm were measured for velocities in the aperture varying continuously from the critical velocity at which stream-line flow ceases and steady eddy motion begins, to the critical velocity at which steady eddy motion ceases and unsteady eddy motion begins.

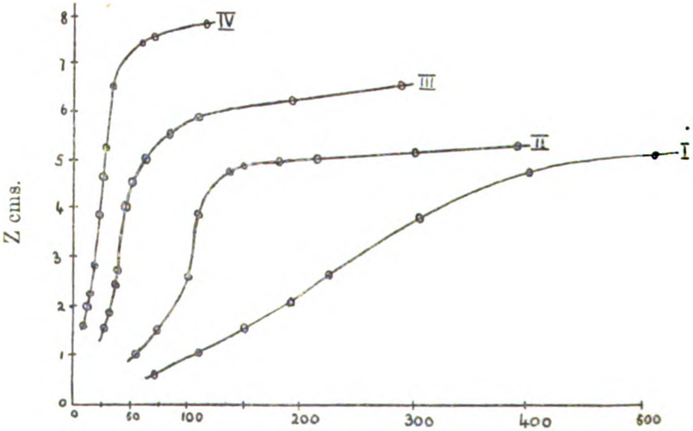
On plotting the longitudinal eddy distances against the mean velocities of the gas in the aperture, each chamber gave a system of four curves (figs. 4 and 5).

Fig. 4.



y (cm./sec.).
Tubular Apertures in Small Chamber.
I. $d = \cdot 052$ cm. II. $d = \cdot 079$ cm. III. $d = \cdot 159$ cm. IV. $d = \cdot 238$ cm.

Fig. 5.

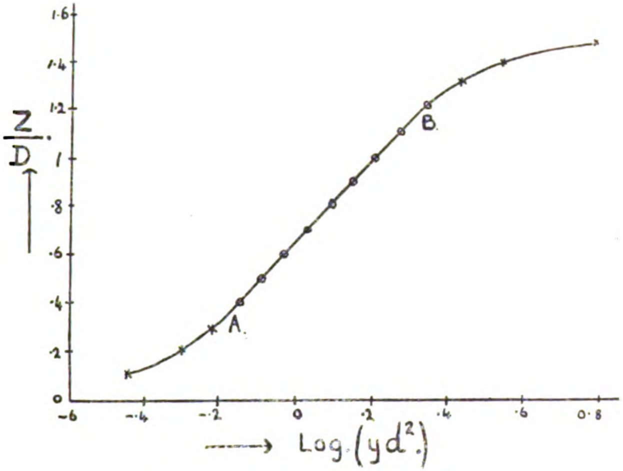


y (cm./sec.).
Tubular Apertures in Large Chamber.
I. $d = \cdot 052$ cm. II. $d = \cdot 079$ cm. III. $d = \cdot 159$ cm. IV. $d = \cdot 238$ cm.

The eddy distance divided by the diameter of the chamber was now plotted against the mean gas velocity in the aperture, and it was found that the curves corresponding to the two chambers coincided.

In order that the variable quantities might be further connected, the quotient of the eddy distance and the diameter of the chamber was plotted against the product of the mean gas velocity in the aperture and the square of the diameter of the aperture; *i. e.*, $\frac{Z}{D}$ against yd^2.

Fig. 6.



AB is Period of Steady Eddy Motion.

In this way the original eight curves were reduced to one curve. A final graph was now drawn in which the logarithms of the previous abscissæ were taken as the new abscissæ. The resulting curve (fig. 6) can be divided into three definite parts:—

I. Velocities less than for steady eddies.

II. Steady eddy motion where $\frac{Z}{D} \propto \log yd^2$.

III. Velocities greater than for II.

For the second part of the curve, which corresponds to the greater part of the experiments (*i. e.*, steady eddy motion) $\frac{Z}{D} \propto \log (yd^2)$, as shown by the straight-line part of fig. 6.

For this part of fig. 6,

$$\frac{Z}{D} + \log A = K \log (yd^2),$$

where A must have the dimensions of (yd^2) and K is a numeric.

Part III.

Velocity Distribution in the Eddies.

In order to study the velocity distribution in the eddies when they were formed, very short exposure photographs were taken, using a full aperture lens and intense illumination. Owing to the difficulties of photography, these were only taken of typical cases. Great care was necessary to obtain successful photographs uniformly illuminated and corresponding to absolutely steady flow. The camera was clamped to a slate bench in order to obtain complete rigidity.

Each smoke particle appears on the photograph as a line, the direction and length of which represent the direction and magnitude of the velocity in the corresponding region of the eddy.

The exposure used was of the order of one-tenth of a second, and of course was varied with the velocities of the eddies, in order to keep the streaks of the photograph to reasonable dimensions and prevent overlapping.

The photographs when obtained were projected, using an ordinary lantern, on to squared paper, using a magnification of about ten times.

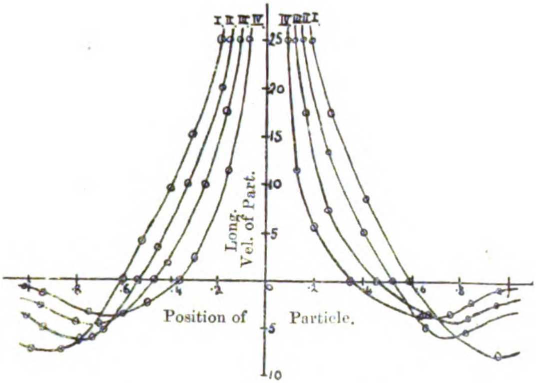
The streaks of the image represent the resultant velocities in both direction and magnitude.

The rectangular components of these were measured, and thus the longitudinal and transverse velocity distributions in the eddies were obtained.

These two velocity components were plotted against the position of the particles in the eddies, using the axis of the chamber (which passes through the aperture) and the line joining the eddy centres as reference axes.

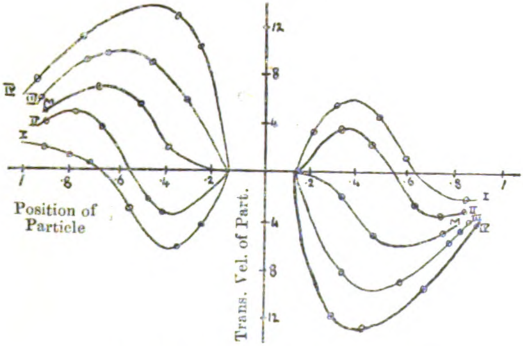
The space between the eddy centres and the diaphragm was divided into four equal spaces by transverse lines drawn at right angles to the axis of the chamber, and the two velocity components along these lines were plotted separately against the position of the particle in the eddies (figs. 7 and 8). The case shown is that of the phenomenon in the smaller chamber at a mean gas velocity in the aperture of 50·6 cm./sec. In the case of the transverse velocity components, an extra section (M) was included midway between the others to show the gradual transition in the shape of the curves.

Fig. 7.



Longitudinal Velocity Distribution.

Fig. 8.



Transverse Velocity Distribution.

Mathematical equations of a two-term exponential type were fitted on to the family of longitudinal velocity distribution curves, using the method of Sir J. J. Thomson (Phil. Mag. xxx. p. 780, 1915).

The equations determined were :—

Curve I. .... $Z = \cdot973$ cm. $v = 61\cdot52\,e^{-5\cdot26(X)^2} - 14\cdot48\,e^{-\cdot857(X)^2}$

Curve II. .... $Z = \cdot730$ cm. $v = 59\cdot17\,e^{-7\cdot52(X)^2} - 10\cdot57\,e^{-\cdot829(X)^2}$

Curve III. .... $Z = \cdot487$ cm. $v = 57\cdot48\,e^{-10\cdot34(X)^2} - 7\cdot41\,e^{-\cdot818(X)^2}$

Curve IV. .... $Z = \cdot243$ cm. $v = 56\cdot08\,e^{-14\cdot88(X)^2} - 6\cdot02\,e^{-\cdot682(X)^2}$

The values of X and D were 1·28 cm. and 2·54 cm. respectively.

It will be seen that the index of the first term on the right of each equation varies inversely as Z, whereas that of the second term is at any rate approximately independent of Z. Hence a single equation which will approximately represent all the cases is :

$$v = 59\,e^{-4\cdot84\left(\frac{X^2}{Z}\right)} - 17\cdot4\,Z e^{-\cdot80(X)^2},$$

where the numbers in the indices must vary inversely as a length and a square of a length respectively. The factor 59 must have the dimensions of a velocity, and the factor 17·4 must have the dimensions of $\left[\frac{1}{T}\right]$. The determination of the way in which they depend on μ, ρ, d, and D requires further experimental examination.

PART IV.

Interaction of Neighbouring Apertures.

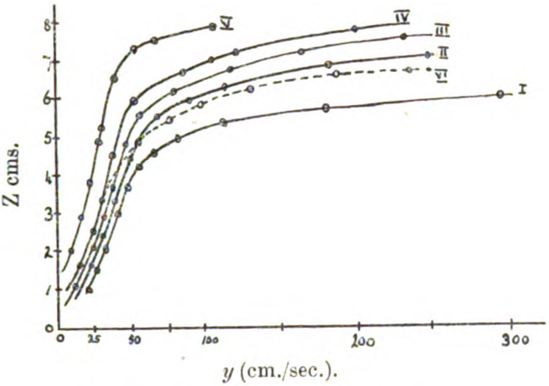
The effect of one aperture being near another was now experimented upon. Diaphragms containing pairs of tubular apertures of ·159 cm. diameter, separated by different distances, were placed successively in the larger observation chamber, and the longitudinal distances of the eddy centres for varying mean velocities of the gas in the apertures measured.

These two quantities were graphed as before (fig. 9) and deductions made from the curves obtained.

The eddies were observed along the line of centres of the pair of apertures, and it was found that the eddy centres' distance was in all cases greater than for a single aperture, and less than the distance for a single aperture of the same area as the sum of the areas of the two apertures and for the same aperture velocity.

The eddies were also observed at right angles to the line of centres of the apertures ; and in this case it was found that, for slow velocities of the gas in the apertures, the eddies were the same distance as in the line of centres, but as the aperture velocity of the gas increased, the two curves separated, though having the same general shape. At right angles to the line of centres of the apertures also, the eddy-centre distance was always greater than the corresponding distance for a single aperture.

Fig. 9.



Interaction of Neighbouring Apertures.

I.	One Aperture.	·159 cm. diam.		
II.	Two Apertures.	·159 cm. diam.	·953 cm. apart.	
III.	do.	do.	·635 cm. apart.	
IV.	do.	do.	·318 cm. apart.	
VI.	do.	do.	do.	[⊥ to line of centres.]
V.	One Aperture.	·238 cm. diam.		

As a general result it was found that when two apertures are separated by eight or nine times their diameter, the effect of one aperture on the other is very small.

Part V.

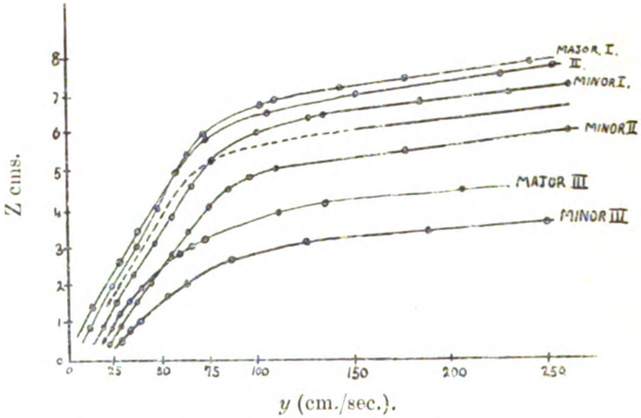
Cylindrical Apertures of Elliptical Cross-Section.

The eddies formed by cylindrical apertures of elliptical cross-section were now examined. Three elliptical apertures were made for the larger observation chamber, each having the same area as a cylindrical aperture of circular cross-section of ·159 cm. diameter, and having as ratios of their major to their minor axes the numbers 1·66, 4, and 10.

The eddies which formed, and the mean longitudinal eddy centre distances, were measured along their major and minor axes for corresponding mean velocities of the gas in the apertures, and the results expressed as before (fig. 10).

The distances measured longitudinally in the plane of the major and minor axes respectively are shown as Major 1, 2, 3 and Minor 1, 2, 3. The dotted curve is that obtained for a tubular aperture of the same cross-sectional area as that of each of the elliptical apertures.

Fig. 10.



Cylindrical Apertures of Elliptical Cross-Section.

Axes of Ellipse. I. ·213 cm. and ·127 cm.
do. II. ·317 cm. and ·080 cm.
do. III. ·506 cm. and ·051 cm.

As will be seen from fig. 10 in the elliptical cases, the eddies observed were not true sections of right circular vortex rings, for although the normal projection of the ring on to the diaphragm was a circle, yet the distance of the ring from the diaphragm was different along different longitudinal sections.

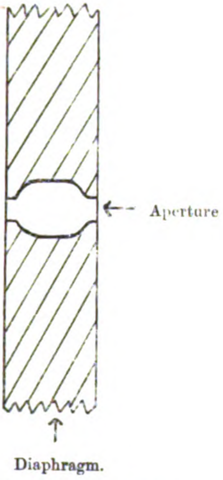
The fact that when the ratio of the axes of the ellipse was nearly equal to unity the phenomena were nearly those produced by two circles having for their diameters the axes of the ellipse, and yet as the axes ratio of the ellipse increased this was not the case, was due to the eddies being initiated at different critical velocities for different diameter apertures.

PART VI.

Non-Cylindrical Apertures.

These investigations were begun with the view of throwing light upon the flow of a gas through the stomata of plants. These stomata are usually non-cylindrical, as well as being elliptical in cross-section. In order to lead up to such cases, apertures with barrel-shaped cavities were constructed for the large observation chamber, and experiments were made with them. Fig. 11 shows a section of such an aperture.

Fig. 11.

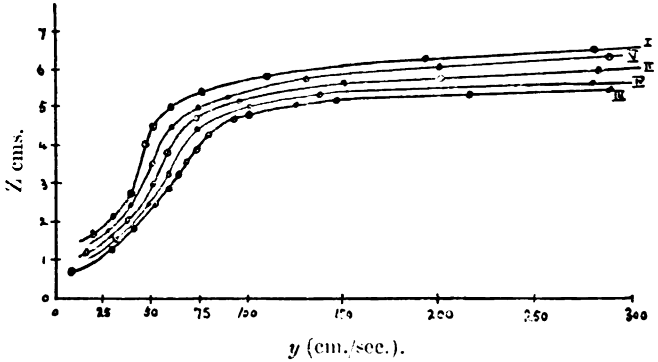


Section of Diaphragm.

Five apertures were made, each having the same diameter at both entrance and exit (=·159 cm.), and having different internal diameters varying from ·159 cm. to 1·27 cm. Each was in turn mounted in the chamber, and the longitudinal distances of the eddy centres measured for various mean velocities of the gas in the aperture.

Again, these two quantities were plotted on a graph (fig. 12). It was found that in no case were the eddy-centres further away from the diaphragm than in the case of a cylindrical aperture of circular cross-section, but varied with the amount of curvature of the section of the aperture. The eddy centres were nearest to the diaphragm when the internal diameter of the aperture was 3·3 times the external diameter, and, when the diameter ratio was greater or less than this number, the eddy-centre distances approached that of the right circular case.

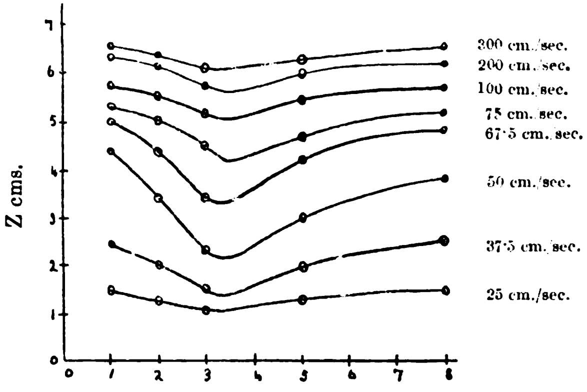
Fig. 12.



Non-Cylindrical Apertures.

Internal Diameter of Aperture :—I. ·159 cm. II. ·318 cm. III. ·477 cm. IV. ·795 cm. V. 1·27 cm.

Fig. 13.



Internal Diameter of Aperture (in $\frac{1}{16}$ of 1 in.).

This was shown very clearly by plotting the eddy-centre distances against the greatest internal diameter of the aperture for eight different mean velocities of the gas in the aperture (fig. 13).

LXX. *A New Determination of the Constant* N *of Avogadro.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I SHOULD like to call to your attention several errors, arithmetical and otherwise, which occur in the interesting paper by Dr. du Noüy, in the October issue of the Philosophical Magazine (Phil. Mag. No. 286, pp. 664–672, "A New Determination of the Constant N of Avogadro, based on its Definition").

1. He states on page 668 that his value $6{\cdot}003 \times 10^{23}$ agrees within 0·1 per cent. with the value found by Millikan ($6{\cdot}062 \times 10^{23}$). Of course this should be approximately 1·0 per cent.

2. He states on page 671 that his probable error is 0·15 per cent., and that therefore his value for N is

$$N = 6{\cdot}003 \pm 0{\cdot}08.$$

This should be

$$N = 6{\cdot}003 \pm 0{\cdot}009.$$

Apparently, his value and that of Millikan agree within the experimental error. Actually, they do not so agree.

3. Three so-called "control" calculations are made on pp. 668 and 669. He states "It is not unnecessary to remark that there is no fallacy whatever in the foregoing reasoning, etc." Elementary considerations show that the three experiments are dependent on one another and that the three "control" calculations are fallacious.

Let

A = surface of adsorption,
m = mass of liquid,
c_1, c_2, c_3 = concentrations of Sodium Oleate in the three minimum surface tension experiments,
ρ = density of Sodium Oleate,
w = molecular weight,
t_1, t_2, t_3 = three dimensions of the molecule,
V = volume of the molecule,
M = the mass of one molecule,
a = horizontal area occupied by a vertical molecule,
n = number of molecules present;

then

$$t_1 = \frac{m}{\rho A} c_1, \quad t_2 = \frac{m}{\rho A} c_2, \quad t_3 = \frac{m}{\rho A} c_3,$$

$$V = t_1 \,.\, t_2 \,.\, t_3 \;= \left(\frac{m}{\rho A}\right)^3 c_1 \,.\, c_2 \,.\, c_3,$$

$$M = \rho\left(\frac{m}{\rho A}\right)^3 c_1 \,.\, c_2 \,.\, c_3,$$

$$a = t_2 \,.\, t_3,$$

$$n = \frac{mc_1}{M} = \frac{mc_1}{\rho\left(\frac{m}{\rho A}\right)^3 c_1 \,.\, c_2 \,.\, c_3};$$

$$na = \frac{\left(\frac{m}{\rho A}\right)^2 c_2 \,.\, c_3 \times mc_1}{\rho\left(\frac{m}{\rho A}\right)^3 c_1 \,.\, c_2 \,.\, c_3} = A.$$

Suppose

$$c_1 \longrightarrow c_1 + \Delta_1,$$
$$c_2 \longrightarrow c_2 + \Delta_2,$$
$$c_3 \longrightarrow c_3 + \Delta_3.$$

Then

$$na = \frac{\left(\frac{m}{\rho A}\right)^2 m(c_1 + \Delta_1)(c_2 + \Delta_2)(c_3 + \Delta_3)}{\rho\left(\frac{m}{\rho A}\right)^3 (c_1 + \Delta_1)(c_2 + \Delta_2)(c_3 + \Delta_3)} = A.$$

To check this, I assumed that the three minima occurred at the same concentration, 10^{-6}, then

$$t_1 = t_2 = t_3 = \frac{mc_1}{\rho A} = 9{\cdot}23 \times 10^{-8} \text{ cm.}$$

volume of molecule $= (9{\cdot}23)^2 \times 10^{-24}$
$= 786{\cdot}3 \times 10^{-24}$ cu. cm.

mass of 1 molecule $= 645{\cdot}55 \times 10^{-24}$ gram.

horizontal space occupied by one molecule
$= (9{\cdot}23)^2 \times 10^{-16} = 85{\cdot}19 \times 10^{-16}$ sq. cm.

molecules in solution $= \dfrac{2 \times 10^{-6} \times 10^{24}}{645{\cdot}55} = 3{\cdot}1 \times 10^{15}$

$$A = 3{\cdot}1 \times 10^{15} \times 85{\cdot}19 \times 10^{-16} = 26{\cdot}41 \text{ sq. cm.}$$

This result is the same as the ones obtained in his control calculations.

Yours truly,

L. M. Alexander,
Asst. Prof. of Physics.

University of Cincinnati.
November 7, 1924.

LXXI. *On the Specific Heats of Carbon Monoxide and Hydrocyanic Acid Vapour.* *By* Prof. J. R. PARTINGTON, *D.Sc.*, *and* M. F. CARROLL, *M.Sc.*[*]

CARBON MONOXIDE.

THE values of C_p, C_v, and γ for carbon monoxide recorded in the literature show little agreement. The earliest measurement is that of Delaroche and Berard[†], who used the method of mixtures, and obtained the value $C_p=8{\cdot}075$ cals. for the temperature range 15°–100° C. Dulong[‡] determined the velocity of sound in carbon monoxide by measuring the frequency of a reed blown by the gas, and comparison with a siren. He assumed the velocity of sound in air to be $V=333$ m./sec., and the variation of velocity with temperature to be $V_t=V_0(1+0{\cdot}00375t)$, where V_t and V_0 are the velocities at $t°$ and 0° C. respectively. Dulong's values require correction for: (1) deviation from the gas laws, and (2) incorrect density values. The value assumed for V_0 in air is also too high: after correction, the value $\gamma=1{\cdot}405$ at 15° C. is found.

Suermann[§] obtained by Delaroche and Berard's method a value for the dry gas, which on recalculation gives $\gamma=1{\cdot}410$ at room-temperature.

Masson[||] improved Dulong's method by using a sonometer wire instead of a siren, and found $V=339{\cdot}76$ m./sec., which on recalculation gives the rather high value $\gamma=1{\cdot}425$ at 15° C.

Regnault[¶] found directly $C_p=6{\cdot}860$ cals., which gives $\gamma=1{\cdot}409$ at room-temperature to 190°.

Cazin[**] improved the Desormes and Clement method by the use of a larger vessel (60 litres), the tap being mechanically operated, and the time occupied in opening and closing the tap (about 0·03 sec.) recorded on a revolving band. He obtained for the diatomic gases N_2, H_2, O_2, CO, etc., the same value $\gamma=1{\cdot}410$. These results require corrections which cannot now be applied, since the constants of the apparatus are not known.

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[*] Communicated by the Authors.

[†] *Ann. Chim. et Phys.* lxxxi. p. 98 (1812).

[‡] *Ann. Chim. et Phys.* xli. p. 113 (1829).

[§] *Ann. d. Physik*, xli. p. 474 (1837).

[||] *Ann. Chim. et Phys.* liii. p. 257 (1858); Phil. Mag. xiii. p. 523 (1857).

[¶] *Mém. de l'Acad.* xxvi. p. 1 (1862).

[**] *Ann. Chim. et Phys.* lxvi. p. 706 (1862); Phil. Mag. xl. pp. 81, 197 (1870).

Wiedemann [*] improved Regnault's method by the substitution of tubes packed with metal turnings for Regnault's heating spiral. The carbon monoxide was prepared from potassium ferrocyanide and sulphuric acid, and probably contained small amounts of impurities, such as hydrocyanic acid vapour, which would tend to give a low result for γ. The value $C_p=6{\cdot}793$ cals., which gives $\gamma=1{\cdot}385$ at 15° C., was found.

Wüllner's [†] work was affected by the presence of impurities, since the experiments themselves are fairly accurate. He used the Kundt method and obtained for the velocity of sound in dry air the accurate value $V=331{\cdot}90$ m./sec. at 0° C. When corrected from modern data, Wüllner's result $\gamma=1{\cdot}403$ gives $\gamma=1{\cdot}401$ for carbon monoxide.

Scheel and Heuse [‡] used an elaborate improvement of the Callender and Barnes constant-flow method. Their results with various gases agree fairly well with those obtained by other methods, although C_p is slightly high in most cases. They obtained for carbon monoxide $\gamma=1{\cdot}398$ at 18° C.

Schweikert [§] employed a slight modification of Kundt's method, but used as the standard gas ordinary instead of dry air. He found $\gamma=1{\cdot}407$, which on correction gives $\gamma=1{\cdot}403$ at 0° C.

HYDROCYANIC ACID.

The only previous measurement of the specific heat of hydrocyanic acid appears to be an approximate determination made by Usherwood [‖], who used the Kundt method at various temperatures from 65° C. to 210° C. As the critical constants of the gas have not been determined, and therefore any equation of state involving their use cannot be applied to calculate the true value of γ obtained, Usherwood employed an empirical equation giving a correcting factor as a function of the observed density:—

$$PV = RT(1+Pf_1(T)+P^2f_2(T)+\ldots).$$

Terms after $Pf_1(T)$ were neglected, and Reech's Theorem then gives:

$$\gamma_{\text{gas}} = \gamma_{\text{air}}\frac{M_{\text{gas}}}{M_{\text{air}}}\left(\frac{\lambda/2 \text{ gas}}{\lambda/2 \text{ air}}\right)^2(1+\alpha)^2,$$

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[*] *Ann. d. Physik*, clvii. p. 1 (1876).

[†] *Ann. d. Physik*, clvii. p. 321 (1876).

[‡] *Ann. d. Physik*, xxxvii. p. 79 (1912); xl. p. 473 (1913).

[§] *Ann. d. Physik*, xlviii. p. 593 (1915); xlix. p. 433 (1916).

[‖] J. C. S. (T.) cxxi. p. 1604 (1922).

where M = molecular weight, λ = wave-length of sound, and $(1+\alpha)$ is the ratio of the observed to the theoretical (ideal) density.

With the rough approximation $C_p - C_v = R = 2$ cals., the theoretical values of γ were calculated, and found to agree remarkably well when the assumptions made are considered. The values obtained by Usherwood are shown in Table VII. at the end of this paper, together with the corrected values. In the correction, the value of γ for air, assumed constant and equal to 1·403 over the range of temperature employed, is taken from 1·403 at 20° C. to 1·397 at 200° C. The use of narrow tubes, which, contrary to the statement of this author, has an appreciable effect on the velocity of sound, is difficult to allow for, since the diminution in velocity due to the radius is not even the same for different gases in the same tube, and in the case under consideration would be appreciable. The assumption $C_p - C_v = 2$ cals. for hydrocyanic acid is probably far from correct at the temperatures employed. This is shown in the case of certain vapours in the tables given by Partington and Shilling *, and especially for water, which bears a strong resemblance to hydrocyanic acid in some of its physical properties. The density factor $(1+\alpha)$ used is also open to criticism, since the experimental densities were apparently obtained on the assumption that the compressibilities of air and hydrocyanic acid are identical, whereas the correction for the deviation from the gas laws for the latter substance is larger than that for air. Vapour-densities determined by the Dumas method, however, can hardly be worth correction. The gas used, obtained by the action of dilute sulphuric acid on potassium cyanide, scarcely fulfils the purity requirements for the determination of physical constants, and there is no mention made of precautions taken to prevent contamination of the vapour by air, due to leakage into the apparatus. It will be obvious that the results obtained by Usherwood, although interesting and useful, can be regarded as approximate only.

Experimental.

The method used, a modification of that of Behn and Geiger, has been fully described in a previous paper †, and only the preparation of the gases will be treated in detail here. All other details of procedure were exactly as described in the reference given.

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* 'Specific Heats of Gases,' p. 204 *et seq.* Benn Bros., Ltd. 1924.

† Partington and Shilling, Phil. Mag. xlv. p. 426 (1923).

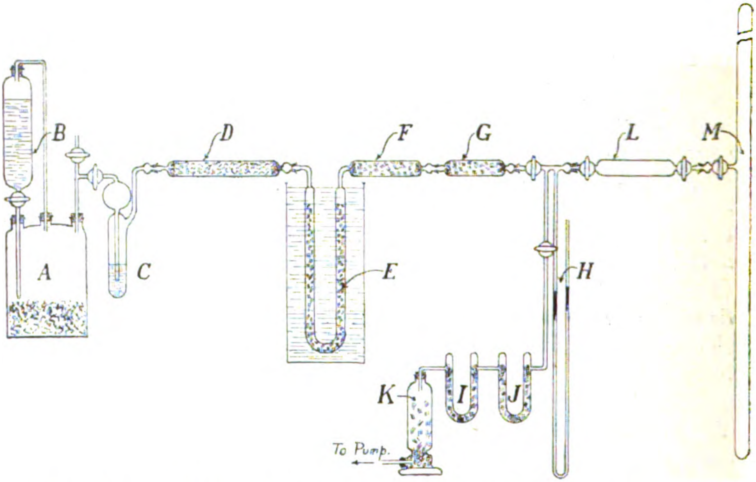
The tube correction factors for the tubes used in these experiments were found by experiment to be :—

Tube A .... Correction factor = 1·0050
„ B .... „ „ = 1·0028
„ C .... „ „ = 1·0071

Preparation of Hydrocyanic Acid.

The apparatus is shown and described in fig. 1.

Fig. 1.



A is a three-necked bottle containing calcium sulphide, B a tap funnel containing dilute hydrochloric acid, C a water bubbler, D a calcium chloride tube, E a tube containing small crystals of mercuric cyanide, immersed in a water bath at 30° C.–40° C., F and G are phosphorus pentoxide tubes, H is a mercury manometer, J a phosphorus pentoxide tube, I a tube containing caustic potash sticks, K a caustic potash tower to absorb the gas, L a sample tube, and M the gas tube.

Pure hydrocyanic acid vapour produced by the reaction :

$$Hg(CN)_2 + H_2S = HgS + 2HCN,$$

passed through the drying tubes G and H which contained phosphorus pentoxide, and then through the sampler L to the gas-tube M. The completeness of the reaction was shown by the fact that while the salt in one limb of the tube E was completely blackened, the crystals in the other limb remained quite white. As an extra precaution a piece of lead acetate paper was inserted in the tube F adjoining the glass joint, and remained unchanged. When the gas-tube had been filled the taps were closed, the tubes removed, and the gas in the sampler L treated with 5 per cent. caustic potash solution, which completely filled the tube. All the joints in the apparatus were of ground-glass, sealed on the outside, when necessary, with Faraday's cement. Before use, the apparatus was evacuated to 10 mm. and allowed to stand overnight; the pressure remained constant. When filling the apparatus any escape of poisonous gas was avoided: (*a*) in the case of carbon monoxide by bubbling through ammoniacal cuprous chloride solution; (*b*) in the case of hydrocyanic acid by leading the vapour through caustic soda solution, and then through the water-pump, the end of which led into the open air.

Results for Hydrocyanic Acid.

The gas-tube was filled as previously described. Measurements were made as in previous experiments, the temperature and pressure being so adjusted that the vapour was well above the point of liquefaction, and the mean value of γ' determined.

The chief difficulty in calculating γ from γ' is the choice of the correction factor. Although the critical constants for hydrocyanic acid are not known, they can be calculated to some degree of approximation for use in a correction term by methods due to P. Walden [*], together with some other empirical relations.

Walden finds the following relation:

$$P_c = K_1 T_s / V_s, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where P_c is the critical pressure, V_s the molecular volume at the boiling-point T_s, and K_1 is a constant. Again,

$$D_c / D_s = K_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where D_c and D_s are the densities of the liquid at the critical point and boiling-point respectively, and K_2 is a constant. These, together with the well-known relations [†]:

$$P_c V_c / T_c = K_3,$$

and

$$T_c / T_s = K_4,$$

give values for T_c and P_c.

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[*] *Zeit. phys. Chem.* lxvi. p. 385 (1909).

[†] Guldberg, *Zeit. phys. Chem.* v. p. 374 (1890).

With an approximate value of T_c we can calculate P_c, or *vice versa*, from van der Waals' vapour-pressure equation :

$$\log P_c/p = f(T_c/T-1), \quad . \quad . \quad . \quad . \quad (3)$$

where f is a constant depending on the nature of the substance. The following values for the constants were calculated for normal and abnormal substances. The former are the values given by Walden, and the latter are those for substances which resemble hydrocyanic acid in certain physical properties, *e. g.* are strongly ionizing media and possess a high dielectric constant :—

	K_1.	K_2.	K_3.	K_4.	f.
Normal substances.........	12·45	2·45	21·8	1·55	3·10
Abnormal substances......	11·35	2·89	18·9	1·695	2·80

Using the data for abnormal substances, with $D_s = 0·690$, we find for hydrocyanic acid,

from (1), $P_c = 87$ atmos. ; from (2), $P_c = 83·7$ atmos. ;

from (3), $P_c = 87·1$ atmos.,

giving a mean of

$P_c = 85$ atmos. approx.,

and hence

$T_c = 506°$ abs.

Using the data for normal substances, we find similarly :

$P_c = 52$ atmos., and $T_c = 464°$ abs.

The values of P_c may be compared with the values for normal and abnormal substances of low molecular weight :

Normal.

Substance............	Air.	N_2.	O_2.	C_2H_2.	CH_4.	C_2H_4.	C_2H_6.
P_c atm. .... =	39·3	33	50·2	68	45·6	50·2	51

Abnormal.

Substance............	HCl.	SO_2.	NO_2.	NH_3.	H_2O.
P_c atm. .... =	82·4	78·9	100	115	217

The *abnormal values* when substituted in the correction term give :

$$\phi = 1·0265 \text{ at } 422 \text{ mm. and } 21°·0 \text{ C.} \quad . \quad . \quad (4)$$

The *normal values* give :

$$\phi = 1·0334 \text{ at } 422 \text{ mm. and } 21°·0 \text{ C.} \quad . \quad . \quad (5)$$

It will be observed that with either correction factor there is fair agreement; thus, with the value $\gamma' = 1·2438$, we find from (4) $\gamma = \gamma'\phi = 1·275$, and from (5) $\gamma = \gamma'\phi = 1·281$. We have adopted the value of ϕ deduced from the *normal* constants, for the reasons given in a later section. A typical specimen of the results is Table I., and Tables II. and III. contain the mean values for the two series of experiments at different temperatures and pressures.

TABLE I.

Hydrocyanic Acid.

Exp. (1). Pressure = 422 mm. T = 21°·0 C.

Tube A. Correction factor = 1·0050.

Air Tube.					Gas Tube.				
No.	A.	B.	Mean.	λ/2 cm.	No.	A.	B.	Mean.	λ/2 cm.
14.	90·6 91·0	90·1 90·5	90·60	6·471					
13.	84·5 84·2	84·4 84·4	84·40	6·492	13.	82·6 82·4	82·0 82·4	82·20	6·323
12.	77·9 77·9	77·8 77·7	77·83	6·485	12.	75·7 75·7	75·8 75·8	75·75	6·313
11.	71·3 71·2	71·3 71·2	71·25	6·477	11.	69·3 70·0	69·0 69·3	69·40	6·309
10.	64·9 64·7	65·1 64·6	64·83	6·483	10	62·7 63·7	62·2 63·8	63·10	6·310
9.	58·5 58·2	58·3 58·4	58·35	6·483	9.	56·5 56·9	56·6 56·9	56·79	6·303
8.	52·2 52·2	51·8 51·8	51·83	6·478	8.	50·7 50·8	50·8 50·2	50·63	6·328
7.	45·4 45·3	45·5 45·2	45·35	6·479	7.	44·1 44·7	43·7 44·0	44·18	6·311
6.	39·3 38·7	38·9 38·7	38·90	6·483					
			Mean	6·482				Mean	6.314

λ/2 for gas corr. = 6·314 × 1·0050 = 6·334 cm.

TABLE II.

Hydrocyanic Acid.

Pressure = 422 mm.

Tube A.

No. of exp.	$\lambda/2$ Dry air. cm.	$\lambda/2$ HCN. cm.	$\lambda/2$ HCN corr. cm.	γ'.	t° C.
(1)	6·482	6·303	6·334	1·247	21·0
(2)	6·502	6·314	6·346	1·246	21·3
(3)	6·494	6·297	6·329	1·243	21·1
(4)	6·511	6·311	6·343	1·241	21·4
(5)	6·484	6·308	6·339	1·248	21·2
(6)	6·491	6·320	6·352	1·249	21·2
(7)	6·518	6·339	6·371	1·249	21·8
(8)	6·515	6·319	6·351	1·243	21·8
(9)	6·538	6·343	6·375	1·244	22·2
(10)	6·537	6·351	6·384	1·247	22·2
Tube C.					
(1)	7·026	6·782	6·839	1·240	20·0
(2)	7·038	6·811	6·858	1·241	20·0
(3)	6·949	6·725	6·772	1·242	19·7
(4)	6·965	6·735	6·781	1·244	19·7
(5)	7·057	6·826	6·873	1·243	20·2
(6)	7·038	6·813	6·860	1·244	20·2
(7)	7·038	6·802	6·847	1·238	20·2
(8)	7·088	6·824	6·873	1·240	20·2

Mean .... $\gamma'=1·2438$ at 20° 80 C.

TABLE III.

Hydrocyanic Acid.

Pressure = 505 mm.

Tube A.

No. of exp.	$\lambda/2$ Dry air. cm.	$\lambda/2$ HCN. cm.	$\lambda/2$ HCN corr. cm.	γ'.	t° C.
(1)	6·473	6·197	6·229	1·211	17·1
(2)	6·481	6·205	6·236	1·209	17·3
(3)	6·484	6·229	6·261	1·218	17·5
(4)	6·486	6·238	6·270	1·222	17·5
(5)	6·479	6·211	6·243	1·215	17·1
(6)	6·469	6·210	6·241	1·217	17·1
(7)	6·486	6·208	6·246	1·212	17·5
(8)	6·487	6·214	6·240	1·212	17·5

Mean .... $\gamma'=1·2145$ at 17·°35 C.

The second series of experiments shows the necessity for keeping the temperature and pressure constant during the experiments. A difference of pressure of 20 mm., or a difference of temperature of 1° C., affects the results to the extent of five units in the third place of decimals, which, in the case of hydrocyanic acid near the point of liquefaction, is greater than the experimental error. A slight decrease of temperature or increase of pressure causes the value of γ to fall rapidly, whereas for "permanent" gases a large increase of pressure causes a comparatively small increase of γ. It is probable that at the second temperature and pressure 17°·35 C. and 505 mm., the vapour of hydrocyanic acid is near its point of liquefaction. Corresponding with the *normal* value of $\phi = 1{\cdot}0334$, we find:

$$C_p - C_v = R\phi' = 1{\cdot}9875 \times 1{\cdot}0713$$
$$= 2{\cdot}130 \text{ cals. at 422 mm. and } 20^\circ{\cdot}8 \text{ C.,}$$

and similarly, for $\phi = 1{\cdot}04024$, we find:

$$C_p - C_v = R\phi' = 1{\cdot}9875 \times 1{\cdot}0880$$
$$= 2{\cdot}160 \text{ cals. at 505 mm. and } 17^\circ{\cdot}35 \text{ C.}$$

Hence at 20°·8 C. and 422 mm.:

$$\gamma = 1{\cdot}281, \quad C_p = 9{\cdot}69 \text{ cals.,} \quad C_v = 7{\cdot}56 \text{ cals.,}$$

and at 17°·35 C. and 505 mm.:

$$\gamma = 1{\cdot}268, \quad C_p = 10{\cdot}22 \text{ cals.,} \quad C_v = 8{\cdot}06 \text{ cals.}$$

for hydrocyanic acid vapour.

Preparation of Carbon Monoxide.

The gas was prepared by the action of pure concentrated sulphuric acid on sodium formate in the cold, and purified by passing through concentrated sulphuric acid, over caustic potash sticks, and over phosphorus pentoxide.

The apparatus was similar to that used for the preparation of hydrocyanic acid, except that tubes containing caustic potash sticks were substituted for the mercuric cyanide tube. The tap tube L was used to sample the gas, which was analysed by absorbing the carbon monoxide in ammoniacal cuprous chloride solution, and any residual gas estimated as air if in sufficient quantity. With the exception of two experiments the gas was completely absorbed, and in the former cases it was shown to contain 0·7 per cent. and

0·3 per cent. of air, respectively. Calculation of C_v shows that these amounts will not affect γ by more than 0·001, *i. e.* about the limit of the experimental error.

Results for Carbon Monoxide.

The tube was filled with the gas and a series of experiments made. It was then refilled and another series taken. When refilling, the tube was only evacuated once or twice, since it was already full of the pure gas. The results were tabulated and the mean value of $\lambda/2$ for the gas tube was then corrected by multiplying by the previously determined tube correction factor for that particular tube; γ' was then calculated from the equation:

$$\gamma'_{\text{gas}} = \gamma'_{\text{air}} \times \left(\frac{M_{\text{gas}}}{M_{\text{air}}}\right) \times \left(\frac{\lambda/2\ \text{gas}}{\lambda/2\ \text{air}}\right)^2.$$

TABLE IV.

Carbon Monoxide.

Exp. (3). $t = 11^\circ{\cdot}5$ C.

Tube A. Correction factor = 1·0050.

Air Tube.					Gas Tube.				
No.	A.	B.	Mean.	λ/2 cm.	No.	A.	B.	Mean.	λ/2 cm.
12.	81·3	81·9	81·53	6·794	12.	82·1	82·7	82·48	6·873
	81·2	81·7				82·4	82·7		
11.	74·3	74·6	74·69	6·782	11.	75·7	75·9	75·60	6·872
	74·4	74·9				75·3	75·5		
10.	67·9	67·9	67·80	6·780	10.	68·5	68·3	68·50	6·850
	67·7	67·7				68·5	68·7		
9.	61·0	61·0	61·05	6·783	9.	62·0	62·3	61·93	6·881
	61·1	61·1				61·7	61·7		
8.	54·2	54·3	54·25	6·781	8.	54·9	54·7	54·73	6·847
	54·5	54·0				54·7	54·8		
7.	47·5	47·7	47·53	6·789	7.	48·5	47·9	48·30	6·886
	47·3	47·6				48·6	48·4		
6.	40·7	40·8	40·70	6·783	6.	41·3	41·1	41·20	6·867
	40·6	4·05				41·2	41·2		
			Mean =	6·785				Mean =	6·869

$\lambda/2$ for gas corr. = 6·869 × 1·0050 = 6·904 cm.

The mean of the experimental values was corrected for deviations from the ideal gas state by Berthelot's equation:

$$\gamma = \gamma'\phi = \gamma'[1 - \tfrac{9}{64}\pi\tau(1 - 6\tau^2)],$$

where

$$\pi = \mathrm{P}/\mathrm{P}_c \quad \text{and} \quad \tau = 1/\theta = \mathrm{T}_c/\mathrm{T},$$

and C_p and C_v were then calculated by means of the equation:

$$C_p - C_v = R\phi',$$

where

$$R = 1{\cdot}9875 \text{ cals.} \quad \text{and} \quad \phi' = (1 + \tfrac{27}{16}\pi\tau^3).$$

A typical series is shown in Table IV., and the final results are tabulated in Table V.

Table V.

Carbon Monoxide.

Pressure = 760 mm.

No. of exp.	λ/2 Dry air. cm.	λ/2 CO. cm.	λ/2 CO corr. cm.	γ'.	t° C.
Tube A.					
(1)	6·779	6·853	6·888	1·403	11·1
(2)	6·784	6·848	6·884	1·400	11·1
(3)	6·785	6·869	6·904	1·403	11·5
(4)	6·778	6·856	6·893	1·402	10·3
(5)	6·776	6·859	6·893	1·405	10·3
Tube B.					
(1)	6·679	6·777	6·795	1·404	9·9
(2)	6·679	6·780	6·798	1·405	9·9
(3)	6·670	6·774	6·793	1·407	9·8
(4)	6·688	6·778	6·795	1·401	10·5
(5)	6·674	6·772	6·789	1·404	9·9
(6)	6·685	6·782	6·801	1·404	10·1
(7)	6·682	6·779	6·797	1·403	10·1

Mean .... $\gamma' = 1{\cdot}4035$ at 10°·3 C.

From the mean values obtained for γ' and t, and the most recent critical data for carbon monoxide *, $P_c = 34{\cdot}6$ atmos., $T_c = 134^{\circ}{\cdot}4$ abs., we find:

$$\phi = 1{\cdot}000675 \quad \text{and} \quad \phi' = 1{\cdot}0053,$$

whence

$$C_p - C_v = 1{\cdot}998 \text{ cals.}$$

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* Cardoso, *J. Chim. Phys.* xiii. p. 312 (1915).

Thence for carbon monoxide at 10°·3 C.:

$$\gamma = 1{\cdot}404\,; \quad C_p = 6{\cdot}940 \text{ cals.}\,; \quad \text{and} \quad C_v = 4{\cdot}942 \text{ cals.}$$

As the values of C_v are practically constant over a small range of temperature, a comparison of the specific heats of permanent gases is rendered fairly simple. The close agreement of the values (all found in this laboratory) of γ, C_p, and C_v for nitrogen and carbon monoxide is shown in Table VI. Nitric oxide, a similar gas in some respects, is also included.

TABLE VI.

Specific Heats of Nitrogen, Carbon Monoxide, and Nitric Oxide.

Gas.	t° C.	M.	N.	γ.	C_p.	C_v.
N_2	16·7	28	10	1·405	6·93	4·93
CO	10·3	28	10	1·404	6·94	4·94
NO	7·6	30	11	1·400	7·00	5·00

N is the number of electrons in the outer shell of the molecule according to the Lewis-Langmuir theory. Results with nitrous oxide and carbon dioxide over a range of temperatures * show that such agreement is purely accidental, and the specific heat is not the same when the molecular weights and hypothetical external electronic structures are identical.

Discussion of the Results obtained for Hydrocyanic Acid.

The question of the applicability of Berthelot's equation of state to associated vapours and the method used in calculating the critical constants may be briefly discussed. Berthelot's equation has been extensively used for the calculation of the specific heats from values of γ' obtained by the velocity of sound and the adiabatic expansion methods, and gives good agreement in both cases when permanent gases are used. In the case of steam, Callendar's empirical equation of state is almost certainly more reliable, but it is not known whether it can be used for other associated vapours. The application of Callendar's equation to the calculation of γ from the experimental values of C_p or C_v leads to results which differ appreciably from those obtained by the use of Berthelot's equation, especially near the boiling-point, as is shown by the following figures for steam * :—

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* Partington and Shilling, unpublished.

At 100° C. Callendar's equation gives $\gamma = 1{\cdot}330$
„ „ Berthelot's „ „ $\gamma = 1{\cdot}310$
„ 200° C. Callendar's „ „ $\gamma = 1{\cdot}312$
„ „ Berthelot's „ „ $\gamma = 1{\cdot}307$

The correction terms deduced from Berthelot's equation and Usherwood's density correction show much greater discrepancies. This is shown in Table VII., together with the experimental results obtained. The actual experimental results for γ' were not given in the paper, but have been calculated by dividing γ by the correcting term $(1+\alpha)^2$.

TABLE VII.

t° C.	ϕ.	$(1+\alpha)^2$.	γ_1.	γ_2.	γ_3.	γ_4.	γ_5.
65	1·0367	1·077	1·214	1·212	1·310	1·308	1·256
100	1·0278	1·041	1·245	1·242	1·296	1·293	1·277
140	1·0199	1·010	1·266	1·262	1·277	1·275	1·288
182	1·0176	1·002	1·248	1·243	1·248	1·243	1·263
210	1·0145	1·001	1·238	1·231	1·238	1·241	1·250

In this table: $\phi =$ Berthelot's correcting term, assuming the values $P_c = 52$ atmos. and $T_c = 464°$ abs.; $(1+\alpha)^2 =$ Usherwood's correcting term; $\gamma_1 =$ Usherwood's experimental γ' values; $\gamma_2 =$ Usherwood's experimental values corrected for variation of γ for air with temperature; $\gamma_3 =$ Usherwood's experimental values using the correcting term $(1+\alpha)^2$, assuming γ for air $= 1{\cdot}403$ (constant); $\gamma_4 =$ Usherwood's experimental values using this correcting term, but corrected for variation of γ for air with temperature; $\gamma_5 =$ Usherwood's experimental values using Berthelot's correcting term and correcting for variation of γ for air.

These results are also represented on the graphs in fig. 2.

Curve I. represents the value of $(1+\alpha)$ obtained from

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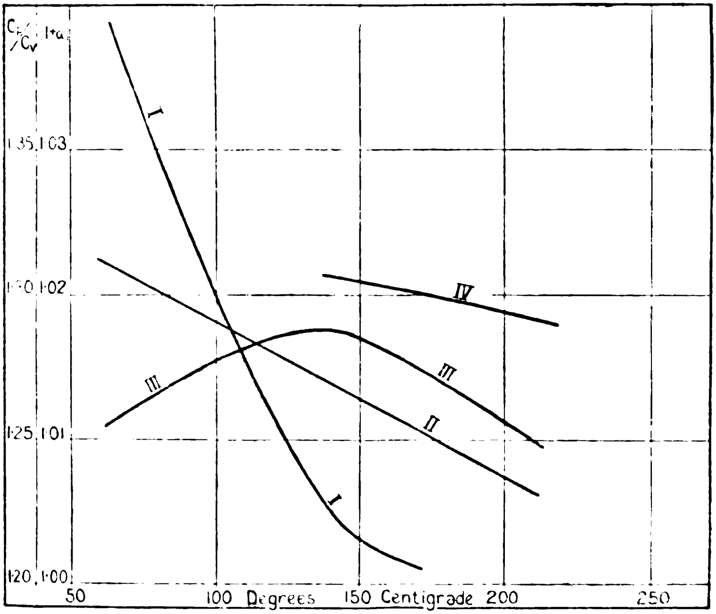
* Partington and Shilling, 'The Specific Heats of Gases,' p. 205.

Usherwood's density results. Curve II. gives the value of γ_4 at different temperatures. Curve III. gives the values of γ_5. Curve IV. gives the value of γ for carbon dioxide at corresponding temperatures.

It will be seen from the above that these results are open to different interpretations, and the factors affecting the results are far more complicated than has previously been supposed.

Fig. 2.



That association accounts for both Usherwood's and the present authors' results appears probable from the following considerations. As we approach the point of liquefaction the greater extent of the association is shown by Curve I., hence the greater are the apparent values of C_p and C_v, since these quantities must be greater for the associated molecules, and consequently the smaller is the value of γ. Thus, Curve III. shows that when the degree of association has become very small the value of γ reaches a maximum, and then decreases in an almost normal manner, as is shown by comparison with Curve IV. for a normal gas (carbon dioxide) at corresponding temperatures. This argument is confirmed by the present results, which show that γ decreases with increase of pressure and decrease of temperature near the point of liquefaction. It will thus be seen that owing to the almost certain existence of association in the gaseous state, a determination of the specific heat of hydrocyanic acid does not necessarily afford any evidence of the existence of tautomerism. The assumption that a change of specific heat with temperature, as such, is to be interpreted as indicating the existence of tautomeric change is, of course, devoid of foundation. A similar difficulty is met with in the attempted determination of the specific heats of nitrogen dioxide, which associates according to the equation :

$$2NO_2 = N_2O_4.$$

This case has been investigated fairly completely, both from the experimental and theoretical standpoint, but even in this comparatively simple case there are many difficulties to be overcome, and the results are far from satisfactory *.

The choice of the correction term ϕ for hydrocyanic acid used by the present authors has yet to be justified. Even if the critical constants for hydrocyanic acid had been experimentally determined, their use in this correcting term would introduce difficulties for the following reasons. From the density measurements the degree of association can be obtained approximately from the equation :

$$\alpha = (D-d)/d,$$

where D is the theoretical density of $(HCN)_2$, d is the observed density of the mixture, and α is the degree of association of the compound $(HCN)_2 = 2HCN$. The equilibrium constant is given by :

$$K = \alpha^2 P/(1-\alpha),$$

and the heat of association, Q, can then be calculated from the equation :

$$\log K = -Q/RT + c,$$

where c is the constant of integration.

Thus, with sufficient data we can find the value of α at any temperature on the assumption that the heat of association is constant over the range employed. Using the density data of Usherwood we calculate, *at the critical point itself*, that α is very small, and therefore the vapour should consist almost entirely of double molecules. Therefore the values of the critical constants experimentally obtained should be mainly those of the substance $(HCN)_2$, which, from the physical point of view, is an entirely different substance from that used in the experiments ; or at least they are those of the simple and double molecules in equilibrium.

The authors have therefore made use of the correction term deduced from the *normal values* of the physical constants of hydrocyanic acid, since, although the vapour is probably associated, the association is small. The association can be approximately estimated by means of the above equations, and was found to be between 5 and 10 per cent. at 20° C. and 422 mm., and between 8 and 13 per cent. at 17°·35 C. and 505 mm. In view of these considerations, the use of the experimental critical constants in the correction terms for associated vapours, such as steam and nitrogen dioxide, must be provisional, since these critical constants, as determined, are merely values for a mixture of the associated and unassociated molecules, and therefore cannot be applied to a mixture under different conditions, which is, in general, of a different composition.

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* Partington and Shilling, 'Specific Heats of Gases,' p. 188.

Whereas the authors' experimental results are considered to be reasonably accurate, the values of γ, C_p, and C_v for hydrocyanic acid deduced from any equation of state must be only approximate, and all values will be "apparent" owing to the effect of such factors as heat of association. The disentanglement of so many complicated factors presents a problem which, although theoretically attractive, is distinctly formidable from the point of view of experimental investigation.

Summary.

The specific heats of carbon monoxide and hydrocyanic acid have been determined by a method depending upon the relative velocities of sound in these gases and in air.

The expected values for the specific heats of carbon monoxide have been confirmed, and some provisional values have been obtained for the ratio of the specific heats of hydrocyanic acid.

TABLE IX.

Gas.	t° C.	P mm. Hg.	$\gamma = C_p/C_v$.	C_p.	C_v.
Carbon monoxide	10·3	760	1·404	6·94 cals.	4·94 cals.
Hydrocyanic acid	20·8	422	1·282	9·69 ,,	7·56 ,,
,, ,, ...	17·35	505	1·268	10·22 ,,	8·08 ,,

The authors are indebted to Mr. W. G. Shilling, M.Sc., for valuable assistance and advice. One of them (M. F. C.) also wishes to thank the London County Council and the Chemical Society for grants which enabled him to carry out the work. The results form part of a Thesis presented to the University of London for the Degree of M.Sc. by M. F. Carroll.

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LXXII. *The Rectification of Alternating Currents by Crystals.*

By ALFRED CLIVE JAMES *.

NO satisfactory explanation has yet been proposed of the property of some crystals of rectifying an alternating current, first discovered by Dunwoody in 1906 †.

Pierce (1907) suggested that the unilateral conductivity of carborundum was due to the small area of contact permitting the passage of electrons more readily in one direction than in the other.

In 1910, Eccles ‡ formulated a purely thermal theory of rectification, based on the Joule effect producing variations in the resistance of oxides and sulphides having large negative resistance coefficients. In 1913 § he deduced a very complete theory from electrothermal considerations. Neither of these theories is satisfactory.

The present attitude is that rectification is due to unilateral conductivity, so that when an alternating voltage is applied, the resulting mean current is a function of the alternating voltage ‖. Up to the present no satisfactory explanation of this unilateral conductivity has been proposed.

J. Strachan ¶ has recently proposed the theory that the loose contact acts as a metallic conductor in one direction and as a dielectric in the other. This seems probable. He then puts forward the hypothesis that the molecules have axes of conductivity, polar in nature and reversible. At the loose contact, changes of polarity, accompanied by actual movements of the molecules, take place. The definite orientation of the surface molecules as determined by crystal structure would result in definite orientation of the conductivity axes, yielding predominant properties in one direction and requiring greater expenditure of electrical energy, in the case of the current in the opposite direction, to reverse the conductivity axes. One pulse of the oscillation passes readily in the predominant direction of conductivity, but the other pulse is met by the dielectric conditions produced by the reluctance of the molecular movements to coincide with the tendency of reversal of the conductivity axes. There seems to be little evidence upon which to base such a theory.

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* Communicated by the Author.

† U.S.A. Pat. Spec. 837616 (1906); Brit. Pat. Spec. 5332 (1907).

‡ Eccles, Proc. Phys. Soc. xxii. pp. 269 and 360 (1910).

§ Eccles, Proc. Phys. Soc. xxv. p. 273 (1913).

‖ D. W. Dye, Dict. of Applied Physics, ii. p. 647 (1922).

¶ Strachan, 'Wireless World,' xiv. p. 245 (1924).

Electrolytic theories were early applied to explain crystal rectification, but so far very little experimental evidence has been produced to support them. In this paper, evidence is brought forward in support of a modification and extension of the old electrolytic theory.

The effect of silver sulphide in increasing the rectifying properties of galena seemed to require investigation. It was also noticed that in addition to possessing unilateral conductivity, on passing a current through a crystal of galena, one contact being a sharp point, the current was not constant. When the point was negative the current invariably rose. When the point was positive the behaviour was less certain. This will be discussed in detail later.

All the crystals used were synthetic, and were prepared by heating precipitated lead sulphide, with or without the addition of other sulphides, with a little sulphur to prevent oxidation, in an electric furnace to 1150° C. and allowing to cool very slowly. The crystals containing stannous sulphide had to be heated to 1250° C.

The Transition Point of Lead Sulphide.

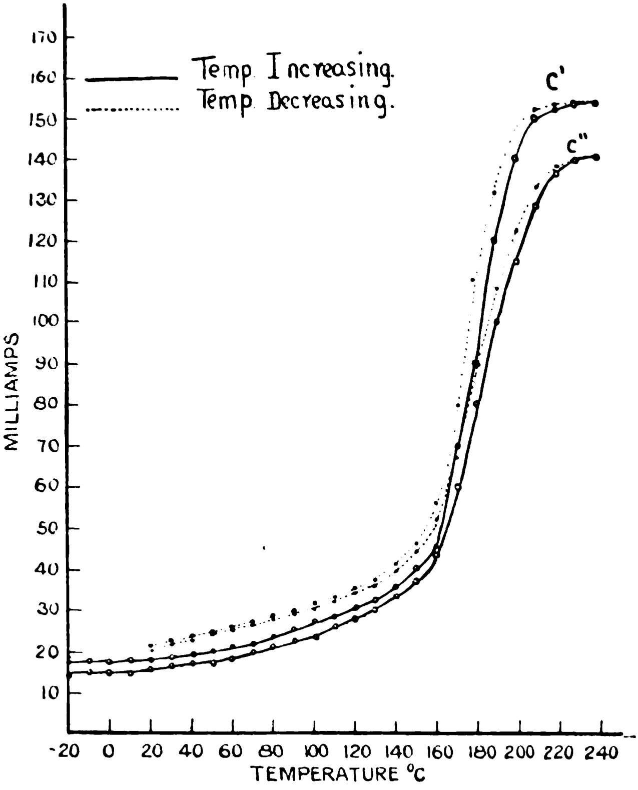
A series of experiments was first carried out in order to find the effect of temperature on the unilateral conductivity of lead sulphide. The crystal was mounted in a brass cup and immersed in pure B.P. paraffin in a large test-tube, this tube also being placed in a bath containing B.P. paraffin. The paraffin immersion ensured the whole crystal being at the same temperature, and also kept the contact clean and free from oxidation. The most satisfactory contact was found to be a fine steel needle fused into a glass tube, connexion being made by mercury in the tube. The glass tube carrying the needle slid easily inside a wider tube, and the pressure of the point on the crystal was constant and approximately equal to the weight of the needle and the tube into which it was fused. A thermometer was also placed in the inner tube.

The crystal was connected in series with a commutator, a milliammeter, and a two-volt accumulator.

On making the circuit, the current passing through the crystal was not constant (*cf.* above). For this reason the current had to be read on the ammeter immediately on completing the circuit, and the current again broken.

The initial values of the current in each direction were plotted against the temperature. The curve is shown in fig. 1. C' is the current when the metallic point is negative, and C'' when positive. C'' was read first, then C'. It was found that the conductivity rose rapidly at 160° C., indicating that galena has a transition point at this temperature. Similar curves were obtained on cooling, but the conductivity never fell to quite its original value. Streintz * (1904) also noticed that on heating a crystal of galena and then cooling, the conductivity was higher than originally. This is probably due to the α-form, stable above 160°, being present in a metastable state.

Fig. 1.



Temperature-Conductivity Curve for Lead Sulphide.

A similar curve was obtained for a crystal consisting

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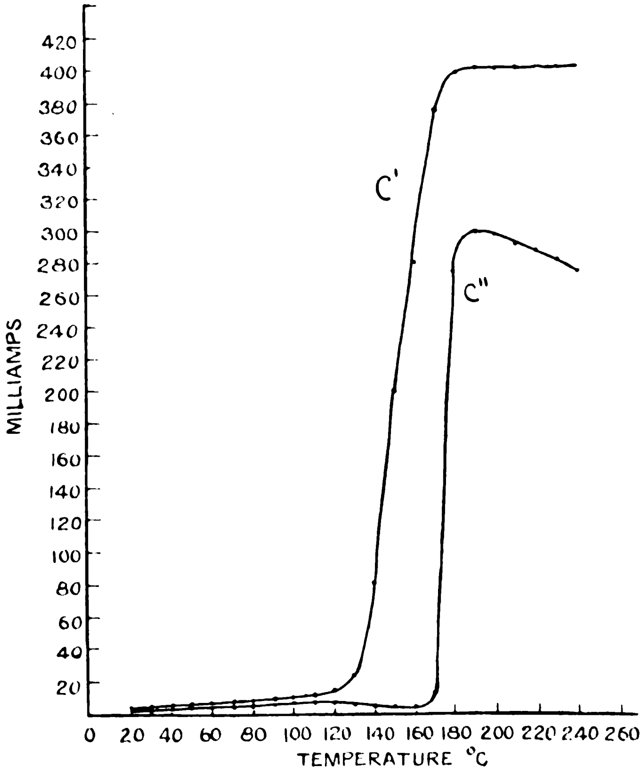
* F. Streintz, *Boltzmann-Festschrift* (1904).

of 90 per cent. lead sulphide and 10 per cent. silver sulphide, but it was found that the increase of conductivity at the transition point was more than trebled. The transition point had been lowered to 133° C. Thus, in the case of pure lead sulphide, the current increased from 45 to 150 milliamps, while in the case of the crystal containing 10 per cent. of silver sulphide it increased from 25 to 400 milliamps. (In this case curve C′ was read before (″) (fig. 2).

Fig. 2.



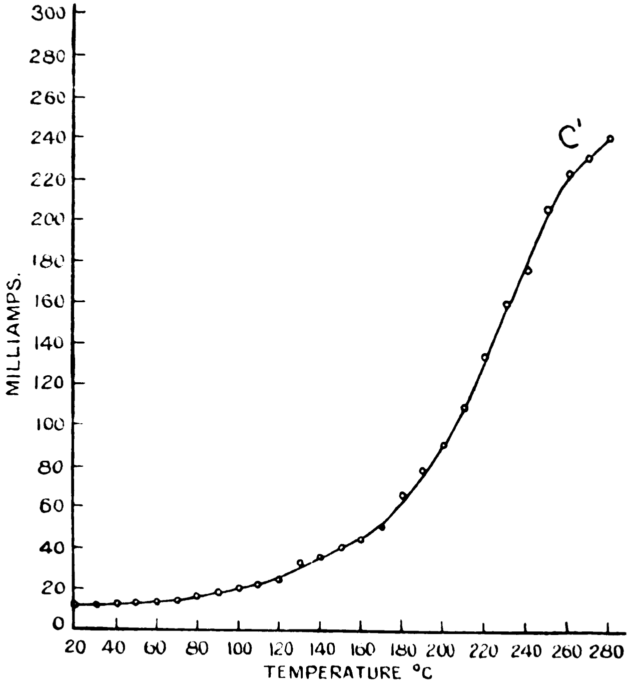
Temperature-Conductivity curves for Lead Sulphide + 10 per cent. Silver Sulphide.

This transition point, at which there is a large increase of conductivity, is similar, but to a less extent, to that which occurs in silver iodide *. At 144°·6 C. the specific conductivity of silver iodide increases from $3{\cdot}4 \times 10^{-4}$ to 1·31.

* Tubandt & Eggert, *Zeit. fur Anorg. Chem.* cx. p. 196 (1920).

A curve was also obtained for a crystal of 95 per cent. lead sulphide and 5 per cent. stannous sulphide. In this case the conductivities in the opposite directions were so nearly equal that only C′ was plotted (fig. 3). With lead sulphide the curve had become nearly horizontal at 210°, with lead sulphide containing 10 per cent. silver sulphide at 180°; but with lead sulphide containing 5 per cent. of stannous sulphide the current was still rising at 270°, the limit to which the paraffin bath could be taken with safety.

Fig. 3.



Temperature-Conductivity curve for Lead Sulphide + 5 per cent. Stannous Sulphide.

This transition point of lead sulphide explains why crystals used for rectifying purposes are most sensitive when cooled very slowly. The usual explanation given is that with slow cooling the sulphide crystallizes better and well-defined crystals are obtained. It has been noticed in connexion with this work that crystals with a granular structure are more satisfactory than those with well-defined faces. A more probable explanation is that unless the crystal is cooled slowly the α-form, stable above 160°, is present in a metastable state.

The Variation of Conductivity with Time.

It has already been mentioned that when a current is passed through a crystal of lead sulphide, one contact being a sharp point, the current is not constant, but if the point is negative, which is the low-resistance direction, rises steadily. The rate of increase decreases with time, and finally the current becomes constant. If the current is allowed to rise for a short time and is then reversed, the current has an initial value approximately equal to that before reversal, and then falls rapidly to the original value in that direction. The rise of the current is always fairly steady, but the fall is often erratic. The current may decrease slowly for a short time, and then fall instantaneously to the initial value.

The rise of current always occurs when the point is the cathode, and this suggests that the phenomenon is of an electrolytic nature. This suggestion is strengthened by the fact that the addition of silver sulphide to the crystal increases the rate and amount of this rise. Silver sulphide is known to conduct 80 per cent. of the current electrolytically below 179°, while above this transition temperature the conduction is wholly electrolytic [*]. If the current is carried electrolytically, it should be possible to detect a difference in weight of the electrode. A silver point weighting 0·03 gm. was used as electrode. It slid easily into a hole drilled in the end of a short piece of brass rod, and was pressed down on the crystal by means of an adjustable spring. The electrode was weighed by means of the torsion type of micro-balance. It was used both as anode and cathode, and crystals of pure lead sulphide and lead sulphide containing 10 per cent. of silver sulphide were used; but even after passing 50 milliamps for 24 hours, the weight of the electrode was constant to within 0·00003 gm., which is within the limits of experimental error. Hence it was concluded that electrolysis, at least of the ordinary type, could not occur. The suggestion arose, however, that the rise of current could be explained by the metal, instead of being deposited on the electrodes, forming metallic threads through the crystal.

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[*] Tubandt & Eggert, *Zeit. fur Anorg. Chem.* cx. p. 196 (1920).

Le Blanc and Kerschbaum[*] have stated that silver sulphide appears to conduct metallically because of the formation of fine threads of silver. The supposed metallic conduction of fused silver halides is also due to threads of silver stretching from pole to pole.

In 1898, Bernfeld[†] stated that the conductivity of lead sulphide increased with temperature. He also pressed lead sulphide between two silver plates and passed a current of one ampere for 20 hours. He found no alteration in the weight of his electrodes. This is similar to the results obtained above for small currents, and is also due to the formation of metallic threads which then conduct metallically. Guinchant[‡] and Aubel[§] (1903) stated that the conductivity decreased with rise of temperature. The differences in these results are probably due to metallic threads forming in Guinchant and Aubel's experiments, the conductivity of these threads decreasing with rise of temperature. Koenisberger[||] (1909) considered that the conduction was metallic. The results given in this paper show that if the currents are momentary, metallic threads have not time to form, and the conductivity then rises with increase of temperature, due to a fraction of the current being conducted electrolytically.

It was found that, although the reversal of the current after it had been passing for a short time was accompanied by a decrease of the current due to the destruction of the metallic threads, if the current in the low-resistance direction was continued until it had become constant, it was found that on reversal, the current in the opposite direction was equal to, or even slightly higher than, that before reversal, and it did not fall. The explanation of this is that after a short time the threads are only formed for a short distance through the crystal, and on reversal the thread becomes the anode and is dissolved; but that when the current has become constant the threads are formed right through the crystal, and the conduction is entirely metallic. The fact that when the current had become constant, the reverse current had a higher initial value than before reversal, is probably due to back E.M.F. No back E.M.F. of polarization could be observed after passing the current for a short time; but this would be due to the fact that, the threads being short, the circuit would be completed through the crystal; but when the threads stretched completely through the crystal, the circuit would be completed through the ammeter, this having the smaller resistance.

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[*] Le Blanc & Kerschbaum, *Zeit. Electrochem.* xvi. p. 680 (1910).

[†] Bernfeld, *Zeit. fur Phys. Chem.* xxv. p. 46 (1898).

[‡] Guinchant, *Comptes Rendus*, cxxxiv. p. 1224 (1902).

[§] Aubel, *Comptes Rendus*, cxxxv. pp. 456 and 734 (1902).

[||] Koenisberger, *Zeit. Electrochem.* xv. p. 97 (1909).

When no current is passing, the threads slowly disappear, provided that the current has not reached a maximum. This can be explained by local electrolytic action in the crystal.

It has already been stated that the current often does not fall steadily, but drops suddenly to nearly its original value. This is due to the metallic threads becoming thinner and then breaking, instead of being dissolved steadily from one end.

At high temperatures the current often rose in both directions. This could be prevented by using a very light contact of thin wire (No. 34 S.W.G.). At high temperatures the pressure of the steel needle is sufficient to prevent the formation of a film at the point, which in this case is the anode, and threads are formed from the other side of the crystal. Threads will be formed very much more easily if the cathode is a sharp point, as the metal will be deposited at the point, and form the beginning of the thread; but it is conceivable that threads might form from the broad contact at the other side of the crystal when the current is large.

It was found that for any one contact the initial rate of rise of the current, and hence the rate of formation of threads, was proportional to the current. The rate of rise varied, however, for different points on the crystal. This will be discussed later. The addition of silver sulphide to the galena increased the rate of rise, while the addition of stannous sulphide decreased it. It was found that with pure lead sulphide the rate of increase per unit current with increase of temperature was constant until the transition point was reached, when it fell rapidly. With galena containing 5 per cent. stannous sulphide it increased to a maximum at 200° and then fell rapidly, showing that in neither case were threads formed above the transition point. With galena containing 10 per cent. of silver sulphide, however, the threads continued to form above the transition point. It is known that silver sulphide conducts entirely electrolytically above 179° *. This therefore is additional evidence that the rise of current is due to the electrolytic formation of metallic threads.

Unilateral Conductivity and Crystal Rectification.

There appears to be a close connexion between unilateral conductivity and the electrolytic formation of metallic threads.

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* Tubandt & Eggert, *Zeit. fur Anorg. Chem.* cx. p. 196 (1920).

The rate of rise of the current varies at different points on the crystal. It was found that when rapid rise of the current occurred there was marked unilateral conductivity. The longer the current was allowed to rise, the more nearly equal became the current in the opposite directions, and the less the rectified current when subjected to an alternating potential difference.

As has already been stated, the addition of silver sulphide to the crystal increased the rate of rise; it also increased the ratio between the opposite currents and the rectifying efficiency. The addition of stannous sulphide decreased the rate of rise, the ratio between the opposite currents, and the rectifying efficiency. These facts all point to unilateral conductivity and the power of rectification being an electrolytic effect. The deposition of metal at the point produces a good metallic contact, and on reversing the current a high-resistance film is formed. Very definite evidence of the formation of this film can be obtained from the graph showing the effect of heat on the conductivity of a crystal consisting of 90 per cent. lead sulphide and 10 per cent. silver sulphide (fig. 2). It will be seen that the curve for C' (C'=conductivity in low-resistance direction, C'' in high) turns upwards at the transition point 133° C. In this experiment the value of C' was read, the current immediately reversed, and C'' read. Between 130° and 170° it was found that on reversing the current the ammeter gave an instantaneous value for C'' nearly equal to C', and then fell at once to the value shown on the graph. This meant that the current, which here increased to a very large value, deposited sufficient metal at the point of contact to cause the reverse current to take an appreciable time to remove this before the high resistance could be formed. Further, the actual strength of the current before the film was formed having increased so much, the film formed was thicker, and though C' rose steeply, C'' actually decreased from 5 to 3 milliamps. At 170° the film was not sufficient to prevent the passage of the current, which immediately increased to 275 milliamps. C' again decreased after the transition point, this also being due to film formation. It was also found that at about 130° to 140°, where this effect was noticed, if C' was kept on for say 5 seconds, on reversal the current kept constant at about the same value as C' for 6 or 7 seconds while the metal was being dissolved, and then fell suddenly as the film was formed. A similar effect was also observed in an experiment, which will be referred to later, on the variation of C'/C'' for different directions through the crystal. In one direction where the ratio C'/C'' was very large it was found that $C''=20$ milliamps. If C'' was kept on for a few seconds and the current then reversed, C' kept nearly constant for a short time and then rose suddenly to 300 milliamps, showing that a high-resistance film was formed when the metal point was the anode, and was removed on reversing the current, the current rising suddenly when the disappearing film was replaced by metallic contact. These observations appear to give definite evidence that a high-resistance film is formed electrolytically when the point is the anode, and metallic contact when the point is the cathode.

It has been stated that for crystals of lead sulphide and lead sulphide containing 5 per cent. of stannous sulphide $\frac{dC}{dT}\cdot\frac{1}{C}$ ($C=$current, $T=$time) falls rapidly above the transition temperature, while it does not do so for lead sulphide containing 10 per cent. of silver sulphide. It was also found that the ratio C'/C'' decreased above the transition point for lead sulphide and lead sulphide containing 5 per cent. stannous sulphide, but did not do so for lead sulphide containing 10 per cent. silver sulphide.

It was found for lead sulphide containing 5 per cent. stannous sulphide and occasionally for pure lead sulphide that the high-resistance direction was not always the same; but when the high-resistance direction was such that the point was the cathode, the difference between the two conductivities was very small; when marked unilateral conductivity occurred, the point was invariably the cathode. It appears that slight unilateral conductivity occurs in these crystals in a direction such that it cannot be explained by the above reasoning. In the following crystals the direction of the rectified current is also such that the point is positive *: molybdenite (MoS_2), galena (PbS) (natural), zincite (ZnO), iron pyrites (FeS_2), cassiterite (SnO_2), and carborundum (SiC). In all these it is interesting to note that the metals readily form amphoteric electrolytes.

Several observers† have noticed a hysteresis effect when the characteristic curve is traced by the steady-current method. On reversing the current and completing the cycle of applied potential, the curve was found to enclose an area. This is explained by the fact that metallic threads are formed, these having to be dissolved again on reversal of the current, thus producing a hysteresis effect.

One of the most puzzling facts in connexion with the

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* Strachan, 'Wireless World,' xiv. p. 397 (1924).

† Pierce, Phys. Rev. xxv. p. 31. Goddard, Phys. Rev. xxxiv. p. 423. Coursey, Proc. Phys. Soc. xxvi. p. 105.

conductivity of crystals is the different behaviour obtained at different parts of the crystal. The rate of rise of the current, the magnitude of the current, the ratio of the conductivities in opposite directions, and the rectifying power or "sensitivity" vary greatly at different parts of crystal surface. This effect is particularly noticeable in the case of a crystal with well-defined faces, and much less so with one with a granular structure and innumerable small facets, when the results are more consistent.

It has been shown by Tubandt * that in solid electrolytes such as the silver halides and silver sulphide the current is carried entirely by the positive ion. Lead chloride differs in that the current is carried by the negative ion. One set of ions in these solids forms a fixed framework through which the other ions move with considerable facility.

Thus in silver sulphide, and most probably in galena, any current which is carried electrolytically will be carried by the metal ion, which will move through a fixed framework of the sulphide ions towards or away from the metallic point.

The structure of a great many crystals has now been determined by several workers. Lead sulphide belongs to the regular system, and usually crystallizes in cubes. It has a simple cubic structure.

In a crystal having such a structure the (100) planes of the crystal each contain both lead and sulphur atoms, the (110) planes will likewise contain lead and sulphur atoms, but the (111) planes, however, will consist alternatively of lead or sulphur atoms

Consider what occurs when the current is being conducted to the metal point along (100) or (110) planes. The metal ions will move towards the point through a fixed framework of sulphur ions; but as they move towards the point they will come into collision with the sulphur ions, and their progress will be retarded. On the other hand, if the current is being conducted along (111) planes, the metal ions will be in one plane and the sulphur ions in the other, and the metal ions will move straight towards the point without colliding with the sulphur ions. Hence, when the current is carried along (111) planes, the metal ions will move with greater facility.

Considering an alternating current passing through the crystal when the current is passing in a direction such that the point is the cathode, metal ions move through the sulphur ions towards the point, giving a metallic contact. On the reversal of the current these ions move away again, leaving a film of sulphur. They will do this with greater facility when the current is carried along planes such that the ions

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* Tubandt, *Zeit. fur Electrochem.* xxvi. p. 358 (1920).

do not collide, and we should then expect to get maximum rectification.

It has been stated by R. Ettenreich[*] that the time of reaction in crystal rectifiers is less than 10^{-6} second, and that this makes electrolytic polarization theories involving comparatively slow molecular movements untenable. In the theory stated above, the film is present continually and the metal ions oscillate to and fro through permanent channels, giving metallic and non-metallic contact alternatively. If the time of reaction is of the order stated by Ettenreich, it is quite in keeping with atomic oscillations of this kind.

Fig. 4.

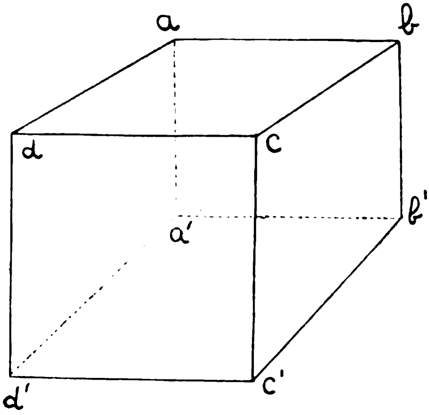

Diagram of a cubic crystal of lead sulphide.

Since the addition of 10 per cent. of silver sulphide increases the rate of formation of metallic threads so considerably, it increases the fraction of the current conducted electrolytically to the same extent, which means that only a small fraction of the current is conducted electrolytically in pure lead sulphide. This fraction causes the alternate metallic and non-metallic contact which has been described, and this rectifies, in addition to itself, that part of the current which is conducted metallically. When the ions move without collision a greater fraction of the current is carried electrolytically. Hence the fraction of the current carried electrolytically varies according to the plane along which the current is passing through the crystal.

Fig. 4 represents a cubic crystal of lead sulphide. According to the theory which has been stated, maximum

[*] R. Ettenreich, *Phys. Zeit.* xxi. p. 208 (1920).

unilateral conductivity (or allied phenomena such as rectification) should be a maximum when the current is carried along (111) planes, *e.g.* when the current passes from *a* to *c* or *b* to *c*′. It should be a minimum when the current passes along (100) or (110) planes, *e.g.* from *a* to *b* or from *a* to *c*′.

With a crystal of pure synthetic lead sulphide, as near a perfect cube as could be obtained, the following results for the ratio of the conductivities in opposite directions were the mean of a number of determinations :—

Current passing from	*a* to *b*	*a* to *c*′	*a* to *c*
Mean ratio, C''/C' ...	1·03 : 1	1·23 : 1	15·9 : 1

These results show that when the current is carried along (111) planes the unilateral conductivity is very much greater than when the current is carried along (110) or (100) planes. This entirely bears out the theory which has been stated.

When a crystal is rectifying high-frequency currents, the ions actually causing rectification will be confined to an extremely thin surface layer at the point of contact, and hence the degree of rectification will depend on the plane along which the current is carried in the surface layer of crystal at the point of contact. Thus with a crystal having an irregular surface maximum rectification will occur at those points where the surface at the point of contact is at such an angle that the current is carried along the (111) planes.

Silver sulphide increases the rectifying power of lead sulphide because it increases the amount of electrolytic conduction, thus increasing the number of ions oscillating in the surface film, and hence the efficiency of the metallic and non-metallic contact. The effect of stannous sulphide in decreasing the rectification is probably due to the fact that it is not isomorphous with lead sulphide, although partially soluble in it. It has a different atomic structure, and its space-lattice will be superimposed upon that of the lead sulphide. Its atoms will therefore obstruct the path of the ions moving in the (111) planes, and hence decrease rectification.

A small applied potential in the same direction as the rectified current improves rectification in most crystals. This is probably due to the fact that the applied potential will assist the formation of metallic threads, but will not be sufficient to prevent the formation of the high-resistance film. Thus it will increase the conductivity of the crystal in the low-resistance direction, but not affect it in the high. In the case of lead sulphide the crystal has a low resistance and the threads are formed rapidly, hence an applied potential does not make much difference. It is a slight advantage, however, but it should be less than one volt. As has been shown, a large potential will cause the formation of permanent threads which destroy rectification.

Strachan * observed that in the rectification of high-frequency currents, when the contact is a loose one and the metal point made from fine wire, oscillation of the point occurs. If a sudden strong current is sent through the crystal, the contact is completely broken. This is easily understandable on the above theory, and is caused by the surging to and fro of the ions. When a strong current is suddenly applied, the amount of metal forced against the point is sufficient actually to move it.

Although in the past electrolytic theories have received little support, and have been subjected to much criticism, the above modification of the old electrolytic theory is based upon experimental evidence, and explains several phenomena which could not be satisfactorily explained by other theories, such as the variation of the rectifying power over the surface of the crystal or "sensitive spots," and the effect of silver sulphide in increasing the rectifying power of crystals of lead sulphide.

Summary.

(1) Galena has a transition point at 160° C., there being an increase of conductivity at this temperature.

(2) Addition of silver sulphide increases the rise of conductivity at the transition point.

(3) Passage of a direct current through galena, the negative contact being a point, is accompanied by the electrolytic formation of metallic threads. This is increased by the addition of silver sulphide and decreased by the addition of stannous sulphide.

(4) Unilateral conductivity, rectification, and electrolytic formation of threads are closely connected.

(5) When the point at the contact is positive a high-resistance film is formed.

(6) Unilateral conductivity and rectification can be explained from consideration of the structure of crystals, and by the fact that in solid electrolytes the current is carried entirely by one set of ions, the other set forming a fixed framework.

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* Strachan, 'Wireless World,' xiv. p. 424 (1924).

(7) In rectification the metal ions oscillate to and fro through fixed channels of sulphur ions, giving metallic and non-metallic contact alternately.

(8) The variation of rectifying properties at different points on the crystal surface can be explained by the fact that the metal ions can move without collision in some planes of the crystal but not in others.

(9) Experimental determinations of the ratio of C′/C″ for different directions through the crystal are completely in accordance with this theory.

(10) Hitherto unexplained phenomena connected with crystal rectification can be explained by this theory.

In conclusion, the author wishes to thank Mr. W. H. Patterson, M.Sc., for his continual interest and help in connexion with this work.

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December 8th, 1924.

LXXIII. *Space-Charge and Thermionic Currents.*

By Wm. S. Kimball *.

The effect of space-charge upon thermionic currents in high vacuum was first treated theoretically by Child † and Langmuir ‡. If the accelerating field was sufficient to cause saturation, assuming the initial velocity of the electrons to be zero, they found that this maximum current varied with the three-halves power of the potential difference between the anode and cathode, and that the potential varied with the four-thirds power of the distance from the cathode. Since then the theory has been extended by Laue §, Richardson ||, Epstein ¶, Fry **, Langmuir ††, and others, taking account of initial velocities or special cases of interest; and Bridgman has treated the theory in its bearing on contact electromotive forces. No attempt seems to have been made to analyse the potential function into its two component parts: the impressed potential and the space charge potential, the former being the potential that would be present

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* Communicated by the Author.

† Phys Rev. xxxii. p. 492 (1911). ‡ Phys. Rev. ii. p. 450 (1913).

§ *Jahrbuch d. Rad. u. Elek.* xv. p. 205 (1918).

|| Em. of Elec. fr. Hot Bodies.

¶ *Ber. d. Deut. phys. Ges.* xxi. p. 85 (1919).

** Phys. Rev. xvii. p. 441 (1921).

†† Phys. Rev. xxi. p. 419 (1923).

between the electrodes in case the space-charge were removed to infinity. The present paper is a critical study of the relations between these two parts of the resultant potential, showing the rôle each plays in the general theory. Attention is restricted to the simple case of currents where the initial velocity of the electrons, that is at the cathode, is zero. The case of parallel plane electrodes is considered in some detail. A special study of the boundary values of the charge density and electron velocity at the anode shows how the equation for the current between parallel plane electrodes may be derived without integrating the differential equation of the potential function. Conditions are established which the exact equation for the current between cylindrical electrodes must satisfy, it being pointed out that the approximate expression given by Langmuir * satisfies them.

§ 1. It is well known that the potential distribution between parallel planes having empty space between them is of the form: $V' = Ex$, where E is the force constant, and that it satisfies Laplace's equation. Since the potential function is a scalar point function, the resultant potential when space charge is present may be separated into its two parts added algebraically: $V = V' + V''$, where V'' is the space-charge potential function. The well-known equations of condition then take the form:

$$1/2\, mv^2 = e(V' + V'') = (Ex + V'')e = Ve. \quad . \quad . \qquad (1)$$

$$i = \rho v. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

$$\frac{d^2V''}{dx^2} = 4\pi\rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad , \quad . \quad . \quad . \quad . \qquad (3)$$

These are the same as those given by Langmuir except for the immaterial change of dropping V' from (3) since its Laplacian is zero. Thus (3) refers to either the space-charge potential or to the resultant potential, but it cannot refer to the impressed potential whose Laplacian vanishes.

§ 2. When ρ and v are eliminated from these three equations we have:

$$\frac{d^2V''}{dx^2} = 2\pi\sqrt{2}\sqrt{\frac{m}{e}}\frac{i}{\sqrt{Ex + V''}}. \quad . \quad . \quad . \qquad (4)$$

Use $2\left(E + \dfrac{dV''}{dx}\right)$ as integrating factor, and integrate:

$$\left(\frac{dV''}{dx}\right)^2 + 2E\frac{dV''}{dx} + E^2 = 8\pi i\sqrt{\frac{2m(Ex + V'')}{e}}. \qquad (5)$$

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* Phys. Rev. xiv. p. 306 (1919).

Here E^2 is the constant of integration, so chosen to give the condition for space-charge limited currents : at the cathode where each potential is zero, the resultant force is zero : $\frac{dV''}{dx} = -E$. Taking the square root of (5) and integrating and solving for i and V gives

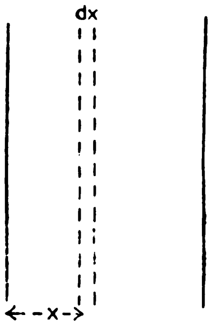
$$i = \sqrt{\frac{2e}{m}} \frac{1}{9\pi} \frac{(Ex + V'')^{3/2}}{x^2}. \quad \text{(6)}$$

$$V = Ex + V'' = cx^{4/3}, \text{ where } c = (9\pi i)^{2/3}(m/2e)^{1/3}. \quad \text{(7)}$$

These equations show that the resultant potential varies with the four-thirds power of the distance from the cathode, and that the space-charge limited current varies with the three-halves power of the resultant potential.

§ 3. *Force due to Space-Charge.*—It is well known that an infinite plane carrying a charge of uniform density, and with no other charges or conductors in its neighbourhood, will exert a force independent of the distance from the plane. If parallel plane conductors are placed at different distances from it, on each side of the uniformly charged plane, there will be induced upon the two conducting planes charges whose density is inversely proportional to their distance from the charged plane between them. If the conductors are at zero potential, the induced charge will be the sole charge on them, and being proportional to charge, the force on each side of the charged plane will thus be inversely proportional to the distance to the parallel conductor. The assumption that the parallel plane electrodes are at zero potential restricts attention to the force due to the space-charge on this plane between them. That the force is

Fig. 1.



inversely proportional to the distance from the electrodes is the outcome of the fundamental principle involved: that equal work is required to take unit charge from either zero potential electrode to the charged plane. If σ_2 is the surface-charge density induced on the cathode and σ_1 is the surface-charge density induced on the anode of a plane of thickness dx and charge density ρ at distance x from the cathode, then the force between this plane and the anode is $4\pi\sigma_1$, and the force anywhere between this plane and the cathode is $-4\pi\sigma_2$. It is noteworthy that the direction is reversed as well as the magnitude of the force operating on an electron changed, as the latter passes through the plane in question.

The space between parallel plane electrodes may be considered as composed of a series of such planes of thickness dx and charge density ρ which latter is constant over each plane but differs for different planes. The sum of the forces due to these planes is the total force due to the space-charge:

$$\frac{dV''}{dx}=\int_0^x 4\pi\sigma_1-\int_x^b 4\pi\sigma_2, \quad . \quad . \quad . \quad . \quad (8)$$

where the σ's are functions of x. The first definite integral gives the sum of the forces due to the several layers of charge behind an electron at distance x from the cathode, that is, it is the total force driving unit charge across. The second integral gives the total force driving unit charge back towards the cathode. Force exerted by the impressed potential is, of course, not included in (8).

Since the potential difference due solely to its own charge between a particular charged plane and each electrode at zero potential is the same, we have a condition on the σ's:

$$4\pi\sigma_2 x-4\pi\sigma_1(b-x)=0, \quad \text{or} \quad \sigma_2 x=\sigma_1(b-x), \quad . \quad (9)$$

where b is the distance between electrodes. A second condition on them is

$$\sigma_1+\sigma_2=\rho\, dx. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The dx appearing in (10) reveals the difference in dimensions of the surface and volume densities. Solving (9) and (10):

$$\sigma_1=\rho\frac{x}{b}\,dx\,;\ \sigma_2=\rho\frac{(b-x)}{b}\,dx. \quad . \quad . \quad . \quad (11)$$

Substituting these values in (8) gives

$$\frac{dV''}{dx}=\int_0^x 4\pi\rho\,\frac{x}{b}\,dx-\int_x^b 4\pi\rho\,\frac{b-x}{b}\,dx. \quad . \quad (12)$$

§ 4. *Boundary Condition upon Force due to Space-Charge.*—If the velocity of the electrons emitted at the cathode is assumed to be zero, then the condition for space-charge limited currents is that the resultant force there due to both space-charge and impressed voltage shall be zero. Since the impressed force is constant between the parallel plane electrodes and equal to E, the boundary condition on the space-charge force at the cathode requires this force to be equal to $-E$. Combining the terms of (12) that involve x explicitly, we may write:

$$\frac{dV''}{dx}=\int_0^b 4\pi\rho\,\frac{x}{b}\,dx-\int_x^b 4\pi\rho\,dx=D-\int_x^b 4\pi\rho\,dx. \quad (13)$$

Here the first term on the right, being a constant, is set equal to D. The value of the space-charge force at a particular distance from the cathode is given by (13) or (12) by giving to the x appearing as a limit in the definite integrals the particular value of the distance in question. Setting x equal to zero in (13) gives

$$\left(\frac{dV''}{dx_0}\right)=D-\int_0^b 4\pi\rho\,dx=-E. \quad . \quad . \quad . \quad (14)$$

This is the boundary condition on the space-charge force at the cathode.

§ 5. *The Space-Charge Potential Function.*—This may be expressed as an integral of (12) or (13):

$$V''=\int_0^x\int_0^x 4\pi\rho\,\frac{x}{b}\,dx\,dx-\int_0^x\int_x^b 4\pi\rho\,\frac{b-x}{b}\,dx\,dx$$

$$=Dx-\int_0^x\int_x^b 4\pi\rho\,dx\,dx. \quad . \quad (15)$$

Equation (9) states that the work due to the particular plane referred to upon unit charge in crossing from cathode to anode is zero. This is the conservation of energy. Equation (15) is the work required to take unit charge from the cathode to distance x due to all of the space-charges. If the upper limit of (15) be set equal to b, the work represented by it will be the sum of such works as represented by (9) for all the space-charge plane layers between the electrodes. Since the work due to each layer of charge upon unit charge crossing to the anode sums up to zero, the work due to all the layers together must sum up to zero. Thus when the upper limit of (15) is b, V'' must be identically zero. This may be shown by integrating the 2nd term by parts:

$$V_b'' = Db - \int_0^b \int_x^b 4\pi\rho\,dx\,dx = Db - \left[\left(x\int_x^b 4\pi\rho\,dx\right)_0^b + \int_0^b 4\pi\rho x\,dx\right] = 0. \qquad (16)$$

The expression in the parenthesis vanishes when the limits 0 and b are substituted, and the last integral is shown by (13) to be equal to $-Db$, so that (16) vanishes identically. This boundary condition on the space-charge potential function is inherent in electrostatics and conservation of energy.

§ 6. *Application of Boundary Conditions for Parallel Plane Electrodes.*—The relations established in § 5 on the space-charge potential may be applied to (7) to get a relation between the constant c appearing in (7) and E, the impressed force. Since $V = V' + V''$, and V'' is zero at the anode, the resultant potential V is at the anode: $V = V' = Eb$. Thus by (7)

$$V = V' = Eb = cb^{4/3}.$$

Hence:

$$c = E/b^{1/3}, \qquad (17)$$

and (7) takes the form:

$$V = Ex + V'' = \frac{Ex^{4/3}}{b^{1/3}}; \qquad (18)$$

hence:

$$V'' = \frac{Ex^{4/3}}{b^{1/3}} - Ex. \qquad (19)$$

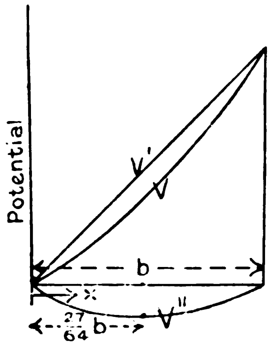
$$\frac{dV''}{dx} = \frac{4}{3}E\left(\frac{x}{b}\right)^{1/3} - E. \qquad (20)$$

$$\rho = \frac{E}{9\pi b^{1/3} x^{2/3}} = \frac{1}{4\pi}\frac{d^2V''}{dx^2}. \qquad (21)$$

The minimum value of V'' occurs where by (20) the force is zero. It occurs at $x = \frac{27}{64}b$, as shown in the graph.

The absolute magnitude of V″ is here 1/4 that of the impressed potential V′ for this value of x. From the cathode out to this point the space-charge opposes the motion of the electrons, but between this point and the anode it expedites their motion.

Fig. 2.



If the potential function appearing in (6) is replaced by (18), the space-charge limited current equation takes the form:

$$i=\sqrt{\frac{2e}{m}}\left(\frac{1}{9\pi}\right)\frac{E^{3/2}}{\sqrt{b}}=\sqrt{\frac{2e}{m}}\cdot\frac{1}{9\pi}\cdot\frac{(Eb)^{3/2}}{b^2}. \quad . \quad . \quad (22)$$

It is noteworthy that this expression is free from the variable x. Its form thus brings out the fact that the current per square centimetre cross-section is independent of the distance of this square centimetre from either electrode, being a constant for changes of x. Since $i=\rho v$, and i is independent of x, the exact equation (22) may be written down if the values of ρ and v at the anode are given: (1) and (18) give v and (21) gives ρ:

$$v_b=\sqrt{\frac{2e}{m}}\sqrt{Eb}\,; \quad \text{and} \quad \rho_b=\frac{E}{9\pi b}. \quad . \quad . \quad (23)$$

The problem of obtaining these boundary values of v and ρ is theoretically a simpler problem than that of obtaining complete information about distribution of potential and charge between electrodes, which is supplied by solution of the differential equation with application of boundary conditions as set forth above. Thus the problem of deriving the exact expression for the saturation current that is constant between the electrodes is theoretically simpler than that of solving the differential equation for space-charge distribution.

§ 7. *Boundary Condition upon the Charge Density.*—It can be shown directly from electrostatics that $\rho_b = \lambda \frac{\mathrm{E}}{b}$, where λ is a pure number, is the expression for the charge density at the anode. To prove this consider equation (3). Since V and V″ are each proportional to the constant E, this equation shows that ρ must also be so. Since b is the only geometrical constant describing the configuration of the electrodes, we may write: $\rho = \lambda \mathrm{E} f(b)$. It is well known that electrostatic force is of the same dimensions as surface-charge density, so that volume charge density or ρ must be of dimensions $\frac{\mathrm{E}}{\mathrm{L}}$ where L stands for length. Since b is the only length involved in the configuration of parallel plane electrodes, it is evident that $f(b) = \frac{1}{b}$ and $\rho_b = \lambda \frac{\mathrm{E}}{b}$, which was to be proved.

The value of the resultant potential at the anode, $\mathrm{V} = \mathrm{V}' = \mathrm{E}b$, together with (1) gives: $v_b = \sqrt{\frac{2e}{m}} \sqrt{\mathrm{E}b}$ for the velocity of the electrons there. Multiplying this by $\rho = \lambda \frac{\mathrm{E}}{b}$ established in this section gives

$$i = \lambda \sqrt{\frac{2e}{m}} \frac{\mathrm{E}^{3/2}}{\sqrt{b}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

This expression for the space-charge limited current is the same as (22) except for a numerical factor, and is obtained without integrating the differential equation (3).

The relations (17)–(21) are obtained from the boundary condition established in § 5 on the space-charge function V″, but if (21) is used to carry out the integrations of § 4, the above relations are seen to be consistent with the boundary conditions established there on the force.

§ 8. *Space-charge Force for Cylindrical Electrodes.*—It is well known in electrostatics that the charge on an insulated hollow cylinder is on the outside, and that within there is uniform potential and no force or charge. If, however, a concentric conducting cylinder within the outer cylinder is grounded, an equal and opposite charge is induced upon the inner cylinder, and the charge on the outer cylinder is transferred from the outside to the inside, and a field is set up between the two cylinders. Likewise if the two cylinders are connected to the two poles of a battery a field is set up between them and the distribution of potential between them is given by $V'=2k \log \frac{r}{a}$, where k is the charge per unit length on one of the cylinders, and a is the radius of the inner one, which may be taken as the cathode, with zero potential, and r is the distance from any point between the cylinders to their axis.

Assume a thermionic current in a steady state flowing between these electrodes. The space between them will contain a series of concentric cylindrical layers of charge. Each layer has uniform distribution of charge upon it, but different layers have different density of charge. Consider a layer of thickness dr and density ρ and distance r from the axis. This layer of negative electricity will induce an equal positive charge on the two electrodes, but not in general an equal amount on each of the two electrodes surrounding the layer. Let σ_1 be the surface density of charge on the outside of the layer in question, and σ_2 that on the inside of this layer. We have:

$$\sigma_1+\sigma_2=\rho\, dr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (25)$$

The charge density induced on the anode will then be $\sigma_1 \frac{r}{b}$ and that induced on the cathode will be $\sigma_2 \frac{r}{a}$, since the areas of the anode and cathode differ from the area of the layer of charge by the indicated proportions. The force due to the layer between the anode and the layer in question is $\frac{4\pi r\sigma_1}{r_0}$, and the force between the cathode and the layer is $-\frac{4\pi r\sigma_2}{r_0}$, where r_0 refers to the place at which the force is measured, being greater than r in the first expression and less in the second. If the potential at each electrode is assumed to be zero, attention is restricted to the effect of the space-charge layer. Equal work will be required to bring unit charge from either electrode to this layer. We have then:

$$\int_r^b \frac{4\pi r\sigma_1 dr_0}{r_0}=\int_a^r \frac{4\pi r\sigma_2 dr_0}{r_0},$$

where r and the σ's are constants for the integration.

$$4\pi r\sigma_2 \log \frac{r}{a}+4\pi r\sigma_1 \log \frac{r}{b}=0. \quad . \quad . \quad . \qquad (26)$$

$$\sigma_2 \log \frac{r}{a}=-\sigma_1 \log \frac{r}{b} \quad . \quad . \quad . \quad . \qquad (27)$$

Solving (25) and (27) for σ_1 and σ_2 gives

$$\sigma_1=\rho\frac{\log\frac{r}{a}}{\log\frac{b}{a}}dr \quad\text{and}\quad \sigma_2=\rho\frac{\log\frac{b}{r}}{\log\frac{b}{a}}dr. \quad . \quad . \quad . \qquad (28)$$

The total space-charge force will be the sum of the forces due to each cylindrical layer of charge :

$$\frac{dV''}{dr}=\frac{4\pi}{r}\int_a^r r\sigma_1-\frac{4\pi}{r}\int_r^b r\sigma_2=\frac{4\pi}{r}\int_a^r\frac{r\rho\log\frac{r}{a}dr}{\log\frac{b}{a}}$$

$$-\frac{4\pi}{r}\int_r^b\frac{r\rho\log\frac{b}{r}dr}{\log\frac{b}{a}}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (29)$$

§ 9. *Boundary Conditions on Force in case of Cylindrical Electrodes.*—Equation (29) may be written :

$$\frac{dV''}{dr}=\frac{4\pi}{r}\left(\int_a^b\frac{r\rho\log\frac{r}{a}}{\log\frac{b}{a}}dr-\int_r^b\rho r\,dr\right); \quad . \quad . \quad . \qquad (30)$$

or

$$\frac{dV''}{dr}=\frac{4\pi}{r}\left(\int_a^b\frac{r\rho\log\frac{r}{b}}{\log\frac{b}{a}}dr+\int_a^r\rho r\,dr\right). \quad . \quad . \quad . \qquad (31)$$

The condition for space-charge limited currents when the initial velocity of the electrons is assumed to be zero is that the force due to the resultant potential be zero at the cathode where $r=a$. This requires that the space-charge force be equal in magnitude and opposite in sign to the force due to the impressed potential at the cathode. This latter force is $\frac{2k}{a}$, so that the boundary condition on the space-charge force is :

$$\frac{dV''}{dr}=-\frac{2k}{a}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (32)$$

The second integral of (31) evidently vanishes when $r=a$, and comparison of the first term of (31) taking $r=a$ with (32) gives the boundary condition :

$$k=-2\pi\int_a^b \frac{r\rho\log\frac{r}{b}}{\log\frac{b}{a}}\,dr=+2\pi\int_a^b r\sigma_2. \quad . \quad . \quad . \quad . \quad (33)$$

The first term of (30) evidently gives the force at the anode due to the space-charge potential function.

§ 10. *Boundary Conditions on the Space-charge Potential for Cylindrical Electrodes.*—Taking account of (33) the integral of (31) may be expressed :

$$V''=-2k\log\frac{r}{a}+\int_a^r\frac{4\pi dr}{r}\int_a^r \rho r\,dr. \quad . \quad . \quad (34)$$

The conservation of energy equation (26) states that the work due to a single layer of space-charge when unit charge is taken from cathode to anode is zero. If the upper limit of V'' in (34) be taken $r=b$ then this equation will represent the sum of such works for all space-charge layers, and must therefore be identically zero. This may be shown by integrating the second term of (34) by parts, taking the upper limit $r=b$:

$$V_b''=-2k\log\frac{b}{a}+4\pi\left(\log\frac{b}{a}\int_a^b\rho r\,dr-\int_a^b\log\frac{r}{a}\,\rho r\,dr\right)=0. \quad (35)$$

The last two terms are seen by (33) to be equal to $2k\log\frac{b}{a}$ which cancels the first term. Thus $V_b''=0$ is the boundary condition on the space-charge potential. Since $V=V'+V''$, this condition is equivalent to :

$$V_b=V_b'=2k\log\frac{b}{a}. \quad . \quad . \quad . \quad . \quad . \quad (36)$$

§ 11. *The Space-Charge Limited Current.*—The current given by equation (2) for parallel plane electrodes and by $i=2\pi r\rho v$ for cylindrical electrodes is constant between the electrodes. Likewise for any shaped electrodes $i=a\rho v$ is constant between them if a is the variable area of cross-section of the tube of flow, or tube between electrodes containing all the current under consideration. The values of ρ and v at the anode, together with the area "a" of the tube which is determined by the geometry of the electrodes, are thus all that is required to set up the equation of the saturation current in terms of the constants of the electrodes in question. The value of v at the boundary is given by equation (1) using the boundary condition established for $V_b=V_b'$: equation (36) for cylindrical electrodes. For a given pair of equipotential electrodes, then, all factors that make up the saturation current are known except ρ_b the charge density at the anode. To obtain this, it would not seem necessary to solve Poisson's equation for the electrodes in question. This method gives the distribution of potential as well as force and charge density *between the electrodes*, a result very much more comprehensive than obtaining merely the charge density at the anode. The problem of obtaining the exact expression for the space-charge limited current in terms of the impressed voltage, and the geometrical constants of the configuration of the electrodes, is therefore distinct from the problem of solving the differential equation obtained by replacing the charge density appearing in Poisson's equation by its value in terms of V by means of (1) and (2). It is distinct and possibly simpler than this latter problem to the extent that obtaining the boundary value of the charge density at the anode is distinct from obtaining complete information as to distribution of charge density, force, and potential everywhere between the electrodes.

§ 12. *Boundary Conditions on the Charge Density for Cylindrical Electrodes.*—The current expressed by

$$i=2\pi r\rho v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

is constant between the electrodes. Equations (36) and (1) give the velocity of electrons at the anode:

$$v_b=\sqrt{\frac{2e}{m}}\sqrt{2k\,.\log\frac{b}{a}} \quad . \quad . \quad . \quad . \quad . \quad (38)$$

If the expression for ρ_b the charge-density at the anode can be obtained in terms of k and a and b, on which it depends, this value of ρ, together with (38), will give the current per unit length of electrode when substituted in (37). The writer has been unable to obtain this expression for ρ_b directly from electrostatics for the cylindrical electrodes, as done in § 7 for parallel plane ones. But the choice of ρ_b is restricted by the following boundary conditions:

(*a*) $\rho_b=kf(a,b)$: it is proportional to k.

This follows from Poisson's equation in cylindrical coordinates, because the first and second derivates of V'' appearing in the left-hand side of this equation are each directly proportional to k, the charge per unit length induced on the electrodes by the impressed potential. Thus ρ appearing as a factor of the right-hand member of Poisson's equation must be proportional to k also. Since a and b are the only geometrical constants involved, ρ_b will depend on some function of them as indicated above.

(*b*) $P=\lambda\frac{k}{L^2}$.

Here L means any length. This condition follows from dimensional considerations since ρ_b is charge per unit volume, and k is charge per unit length. λ is a pure number.

(*c*) When $a=b=\infty$, $\rho_b=\lambda\frac{E}{b-a}$.

When the radii of curvature of the cylindrical electrodes are infinitely large, we have parallel plane electrodes, so that ρ_b must reduce in this case to expressions found in §6, and §7, which are equivalent to (*c*) when $b-a$ is the distance between electrodes.

(*d*) When $a=0$, $\rho_b=0$.

As the size of the cathode approaches zero, the current emitted will evidently approach zero, and hence the charge density at the anode will approach zero.

§ 13. *Form of Expression for Charge Density satisfying the Conditions of* § 12.—It is not difficult to show that the above conditions are satisfied by any ρ_b of the form :

$$\rho_b=\lambda\frac{k}{b^2 f\left(\log\frac{b}{a}\right)}, \quad \ldots\ldots \quad (39)$$

where $f\left(\log\frac{b}{a}\right)$ refers to any function of $\log\frac{b}{a}$ expressible as a power series in $\log\frac{b}{a}$, whose constant or zero power term is lacking, and also whose first power term is present, such as simply $\log\frac{b}{a}$ itself, or $\left(\frac{b}{a}-1\right)$.

The current equation of Langmuir :

$$i=\frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\frac{V^{3/2}}{b\beta^2},$$

where

$$\beta=\log\frac{b}{a}-\frac{2}{5}\left(\log\frac{b}{a}\right)^2+\frac{11}{120}\left(\log\frac{b}{a}\right)^3\ldots.$$

shows in view of (36), (37), and (38) that his ρ involved in this current equation is of the form (39).

The writer is much indebted to Prof. W. F. G. Swann and Mr. E. S. Akeley of Chicago for valuable criticism and discussions.

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LXXIV. *On Molecular Diameters.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a paper published in your November number of 1924 on "The Determination of Molecular Diameters," Mr. Sergius Mokroushin deduces a formula for the diameter which includes the following reasoning: The internal heat of vaporization of a gram-molecule is equal to the product of the surface-tension and the surface of all its molecules. The molecules are thus assumed to be liquid droplets having the same surface-tension as the liquid itself. In a paper just published [*] I have calculated molecular diameters starting also from a relation between heat of vaporization and surface-tension, using the modern point of view on constitution of matter.

All methods of this determination, which are founded on phenomena caused by molecular collision, give values of the diameter depending upon the momentum of the colliding molecules. The greater their velocity is and the higher consequently (in cases to be discussed) the corresponding temperature is, the smaller such a diameter turns out. It is called recently "Stossdurchmesser" in German, which may be translated by "collisional diameter." The method I used gives collisional diameters and was employed in order to determine them at a temperature as low as possible.

It is now shown [†] that surface-tension consists of a statical portion χ, independent of molecular motion, and of a kinetic portion dependent upon temperature and vanishing in the limit to the absolute zero. Therefore we may write for χ_0, the statical portion at the absolute zero, using the relation of Ramsay and Eötvös

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[*] *Zeitschr. f. Physikalische Chemie*, cxiv. p. 114 (1925).

[†] Madelung, *Physikalische Zeitschr.* xiv. p. 729 (1913). Born und Courant, *Physikalische Zeitschr.* xiv. p. 731 (1913).

$$\chi_0 = \frac{2{\cdot}1\mathrm{T_K}}{\mathrm{V}_0^{2/3}}, \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

where $\mathrm{T_K}$ is the critical temperature and V_0 the molecular volume at the absolute zero.

As to the constitution of the molecule we assume that it is in case of non-associating substances an electric quadruple. That is a neutral aggregate of positive and negative charges whose centres coincide in absence of a field. In a field f it is deformated and acquires a momentum αf, α being a molecular constant. τ is also a molecular constant determined by the configuration of the charges. These assumptions were made by Debye * in order to explain the v. d. Waals forces. In the same paper he calculates the statical portion of surface-tension as the mechanical work required to build up the unit area of the surface, not regarding it as a monomolecular layer, and finds

$$\chi = \frac{3\pi}{8}\,\frac{\alpha\tau^2 n^2}{s^4}, \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

where n is the molecular density and s the molecular diameter considered as collisional as follows from Debye's reasoning. He determines also Λ, the internal heat of vaporization for one gram-molecule in C.G.S.-units, by the same quantities. From his formula we obtain

$$\Lambda = \frac{6\pi}{5}\,\frac{\alpha\tau^2}{s^5}\,n^2\mathrm{V}, \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where V is the molecular volume at boiling-point.
From (2) and (3) we obtain

$$s = 3{\cdot}2\,\frac{\chi\mathrm{V}}{\Lambda}. \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

Since from (2) $\chi \sim n^2 \sim \frac{1}{\mathrm{V}^2}$ we get from (4) by use of (1)

$$s = 6{\cdot}72\,\frac{\mathrm{T_K}}{\Lambda}\,\frac{\mathrm{V}_0}{\mathrm{V}}\,\mathrm{V}_0^{1/3}. \quad . \; . \; . \; . \; . \; . \quad (5)$$

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* *Physikalische Zeitschr.* xxi. p. 178 (1920).

Assuming the closest packing of molecules at the absolute zero, so that $V_0 = \frac{L}{\sqrt{2}} s^3$, and putting $V = \frac{M}{D}$,

$$\Lambda = M\lambda_i 4{\cdot}18 \,.\, 10^7,$$

where

D = the density of the liquid at boiling-point,
M = the molecular weight,
λ_i = the internal heat of vaporization for one gram in cal.
L = Loschmidt's number, the number of molecules in one gram-molecule,

we find from (5) for the molecular diameter in centimetres

$$s \,.\, 10^8 = \sqrt[3]{0{\cdot}184 \frac{M^2\lambda_1}{T_K D}} \,. \quad . \quad . \quad . \quad . \qquad (6)$$

The following table gives values for s calculated by (6) and also values for s^*, the diameter on the dynamical theory

Table I.

Substance.	$s \,.\, 10^8$.	$s^* \,.\, 10^8$.	$\frac{s}{s^*}$.
Helium	3	1·9	1·6
Hydrogen	3·1	2·3	1·3
Nitrogen	3·9	3·1	1·3
Carbon monoxide	3·9	3·2	1·2
Argon	3·6	2·7	1·3
Oxygen	3·6	2·9	1·2
Carbon dioxide	4·0	3·2	1·3
Nitrous oxide	4·0	3·1	1·3
Methyl chloride	4·5	3·4	1·3
Chlorine	4·3	3·7	1·2
Iso-pentane	6·4	4·5	1·4
Ethyl ether	6·2	4·8	1·3
Acetone	5·8	3·8	1·5
Methyl acetate	5·8	3·8	1·6
Ethyl acetate	6·4	4·2	1·5
Chloroform	5·7	4·8	1·5
Benzene	5·9	4·1	1·4
		Average...	1·37

of gases. For its evaluation the formula for viscosity was used which Chapman, and independently of him Enskog, has deduced. This formula accounts for intermolecular forces and gives also collisional diameters. But they correspond to a temperature much higher than the diameters calculated by (6). According to that the values for s^* are smaller than the values for s in the average about 30 per cent.

The molecule being identical with the atom in the case of argon, we may compare its value for s with the value for the atomic diameter which is calculated by the formula of Eucken-Lindemann †, giving a collisional diameter corresponding to the melting-point. Assuming that the crystalline argon has a face-centred cubic lattice as proved from X-ray measurement by Simon and v. Simson ‡, we obtain for the diameter $3{\cdot}6 \times 10^{-8}$ cm. in perfect accordance with the value from (6). The corresponding temperatures are practically identical, the melting-point being 85° K and the boiling-point to which (6) relates 87° K.

Institut f. theoretische Physik
an der Universität, Vienna.
Jan. 20, 1925.

Yours faithfully,
H. SIRK.

LXXV. *Variation of Logarithmic Decrement with Amplitude and Viscosities of certain Metals.* By G. SUBRAHMANIAM, *M.A., A.Inst.P.*, and D. GUNNAIYA, *M.A., A.Inst.P.*§

Introduction.

WITH a view to determine the absolute coefficient of viscosity of certain liquids by oscillating a solid of "easy" shape, the authors have used a fine copper wire as suspension and have noticed remarkable variation of logarithmic decrement with amplitude. The results are not quite in agreement with those obtained by others, and could not therefore be represented by any one of the empirical formulæ proposed. They have therefore instituted a series of experiments to study, at some length, the nature of variation of logarithmic decrement with amplitude and, if possible, to correlate it with other elastic properties of the material. The results obtained seem of sufficient general interest to merit publication, and the authors therefore propose to set

† Eucken, *Grundriss der physikalischen Chemie*, p. 342.
‡ *Zeitschr. f. Physik*, xxv. p. 160 (1924).
§ Communicated by Prof. E. H. Barton, F.R.S.

forward the results of their experiments, in the first instance, with copper, brass, and steel wires.

The change of both the logarithmic decrement and the period with amplitude has, of course, long been recognized. Schmidt[*] and, later on, Voigt[†] have found that the logarithmic decrement varies approximately as the square of the amplitude, while Streintz[‡] found it to be independent of the amplitude in torsional vibrations and also of the period. Guthe and Sieg[§], experimenting with certain platinum iridium wires, found that the decrement amplitude curves show a maximum value, and that this value depends on the initial amplitude. Harris[‖], on the other hand, using bismuth wires, observed a decrease of the logarithmic decrement with decreasing amplitude, but no maximum or minimum values. George A. Lindsay[¶] concluded that the decrement of longitudinal vibrations of wires made of copper is proportional to the amplitude, and that the increase for other metals is less regular.

Such behaviour of wires is influenced to a marked extent by (i.) internal friction and (ii.) elastic fatigue or after-effect; and accordingly either or both of these causes is supposed to account for the observed differences in the rates of subsidence of vibrations. If the damping is caused by the elastic after-effect, the logarithmic decrement, according to Boltzmann's theory, is independent of the period; and if there is really internal friction, the decrement depends on the period. The results of Voigt's[**] work were not entirely in favour of either theory, and his conclusion was that in some cases the preponderant factor in damping is internal friction, in other cases it is the after-effect.

The viscous resistances called into play when a wire is set in vibration and to which the decay is largely due do not seem to be of the ordinary type; that is to say, such as are proportional to the rates of strain. If this type of resistance alone were involved, the proportionate diminution of the amplitude of oscillations per unit of time, as Lord Kelvin[††] pointed out, would be inversely proportional to the square of the period.

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[*] Wied, *Ann.* ii. p. 48 (1877).

[†] *Abh. der Konigl. Gesell. der Wiss. zu Göttingen*, xxxviii. p. 189.

[‡] *Wien. Ber.* lxix., II. Abt. p. 337 (1874); lxxx., II. Abt. p. 397 (1879).

[§] Phys. Rev. xxx. no. 4 (1910).

[‖] Phys. Rev. xxxvi. no. 2 (1912).

[¶] Phys. Rev. June 1914.

[**] *Loc. cit.*

[††] 'Mathematical and Physical Papers,' iii. p. 27.

Besides these two chief causes, the dissipation of energy from the point of suspension * outwards also, perhaps, partly accounts for the variation of decrement with amplitude.

Experiments.

On the present occasion wires made of three different materials—namely, copper, brass, and steel—are used. In each case experiments are conducted with wires of different thicknesses and of different lengths. In view of the large amount of attention which the study of elastic properties of copper wires received at the hands of Lord Kelvin †, Joseph O. Thomson ‡, and several others, it is thought desirable to experiment with a greater number of wires made of copper than of the remaining two. These copper and brass wires are taken from ordinary commercial spools supplied by an electric warehouse, and are therefore of doubtful composition; the steel wires are, however, the best piano wires from Misquith and Co.

Each of these wires before it is experimented on is kept stretched by half the maximum load which it can carry for the given dimensions, and is allowed to remain in that condition for several days. The wire is then suspended in an air-free chamber to the top of a massive stand by means of a self-centering three-jawed chuck, the lower end being fixed to a rotating cylinder by a similar device. Before readings are taken it is found necessary to bring the wires to a steady state. In the initial stages no two consecutive sets of readings agreed closely, so that the wires were kept in a state of continuous vibration for, indeed, a pretty long time before perfect consistency could be achieved. Thus in the case of the thinnest copper wire the values for the logarithmic decrement for a *given amplitude* progressively diminished with each successive trial, until at last it tended to a constant value. The time for which these wires should be kept thus continuously vibrating before constancy is obtained is, however, different for different metals, and even for the same metal it is found to increase with cross-section.

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* Kôtarô Honda and Seibi Konno, Phil. Mag. July 1921: and Iokibe, Phil. Mag. Sept. 1921.

† *Loc. cit.*

‡ Phys. Rev. March 1899.

For copper this interval is about three to five hours, for brass about six to ten hours, whereas for steel it is as great as five to seven days.

A small bit of mirror is attached to the wire immediately above the lower chuck, and the wire in addition carries a fine pointer bent vertically down at the back of the mirror. The successive amplitudes are read off by the usual telescope and scale method, and for appreciable values this method, though simple, is found to answer exceeedingly well, as a sufficiently quick and trained eye can read correctly to a tenth of a millimetre. When the extent of the swing has fallen to about a centimetre the following method is adopted. A telemicroscope having in its eyepiece a scale divided into tenths of a millimetre is focussed on the vertical pointer behind the mirror, and is permanently arranged on the other side of the telescope and scale. The extent of the swing of the pointer is read off on the scale within the eyepiece. Readings so obtained are correct to a hundredth of a millimetre, as will be seen from the experimental results tabulated below.

One peculiarity which the authors have noticed in the course of these experiments deserves special mention, though it may be a repetition * of what others engaged in similar work have observed. For a particular length of one of the copper wires the amplitude is found to diminish gradually, and after a time, strangely enough, the values increase, and this progressive rise and fall is quite periodical and lasts for a considerable length of time. At the same time it is observed that the torsional pendulum begins to make pendulous oscillations, though, to start with, the vibrations are purely torsional. These pendulous oscillations are again noticed to die down, to be reborn again, and so on. This anomalous behaviour is evidently due to the mutual transference of energy from torsional to pendulous oscillations and *vice versa*, and arises from the synchronization of the two periods—a fact so conspicuous in the theory of resonance.

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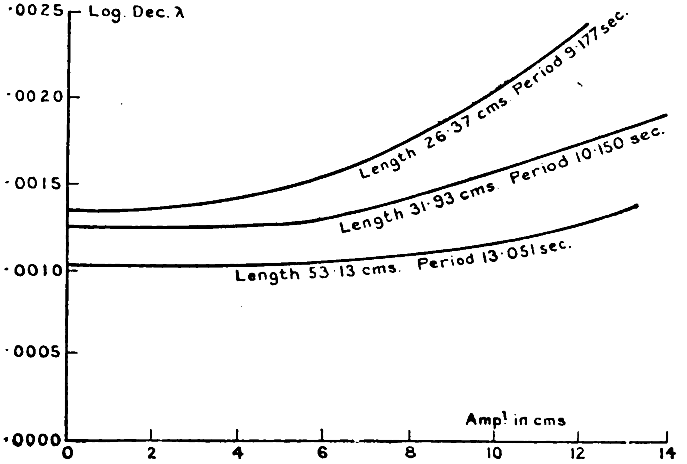
* Herbert Tomlinson, Proc. Phys. Soc. August 1886.

Experimental Results.

Copper Wire, diam. 0·03302 cm. (Graph No. 1.)

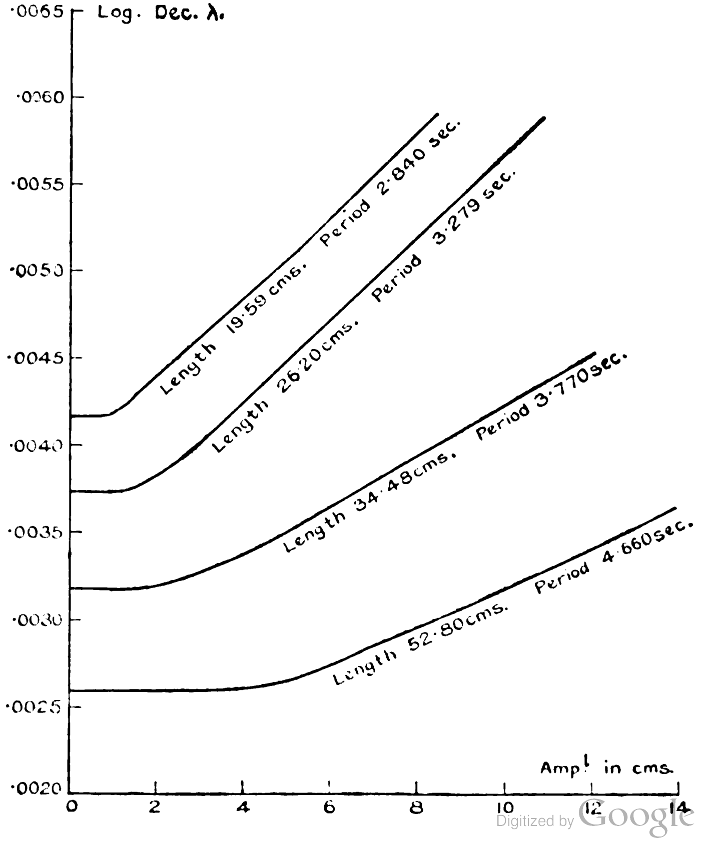
Length, 53·13 cm. Period, 13·051 sec.		Length, 31·93 cm. Period, 10·15 sec.		Length, 26·37 cm. Period, 9·177 sec.	
Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.
13·20	0·001394	14·00	0·001901		
12·37	1321	12·81	1808		
11·01	1238	11·62	1701	11·40	0·002334
9·80	1171	10·50	1669	10·23	2129
8·30	1109	9·63	1554	9·27	1915
7·54	1094	8·87	1501	8·58	1871
6·80	1082	7·58	1411	7·82	1750
6·13	1071	6·60	1335	6·43	1582
5·50	1062	5·95	1305	5·60	1529
4·86	1051	5·13	1284	5·03	1490
4·15	1049	4·24	1272	4·75	1471
3·64	1045	3·80	1261	4·12	1436
3·20	1047	3·02	1257	3·84	1417
2·90	1043	2·45	1253	3·23	1386
2·20	1045	2·00	1250	2·42	1361
1·45	1042	1·63	1249	1·95	1353
1·00	1046	1·21	1251	1·50	1350
·812	1049	·771	1253	·778	1352
·631	1045	·603	1248	·601	1349
·504	1044	·382	1251	·417	1348
·235	1043	·219	1251	·239	1348

Graph 1.



Copper Wire, diam. 0·0555 cm. (Graph No. 2.)

Length, 52·8 cm. Period, 4·66 sec.		Length, 34·5 cm. Period, 3·77 sec.		Length, 26·2 cm. Period, 3·28 sec.		Length, 19·6 cm. Period, 2·84 sec.	
Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.
15·10	0·003710						
13·23	3508	12·00	0·004551				
11·72	3350	11·02	4408	11·21	0·005982		
9·80	3142	9·83	4245	10·13	5709		
8·48	2996	8·51	4052	9·40	5501		
7·10	2874	7·20	3860	8·60	5364	8·52	0·005936
6·30	2802	6·41	3748	7·82	5204	7·30	5658
5 12	2694	5·41	3600	6·56	4904	6·32	5426
4·78	2670	4·87	3532	5·71	4710	5·12	5142
3·65	2637	3·64	3388	5·12	4560	4·40	4971
3·15	2620	3·00	3312	4·30	4358	3·48	4746
2·80	2616	2·13	3250	3·47	4169	2·50	4524
2·50	2614	1·60	3231	2·91	4048	2·13	4431
2·18	2614	1·12	3210	2·63	3984	1·62	4314
1·70	2615	·83	3204	2·30	3910	1·19	4224
1·30	2610	·61	3170	1·91	3859	·90	4220
1·02	2614	·38	3202	1·50	3808	·75	4200
·80	2615	·31	3201	1·13	3771	·62	4197
·62	2614	·20	3202	·82	3760	·50	4190
·53	2614			·55	3760	·38	4191
·35	2613			·52	3758	·23	4190
·28	2610			·33	3764		

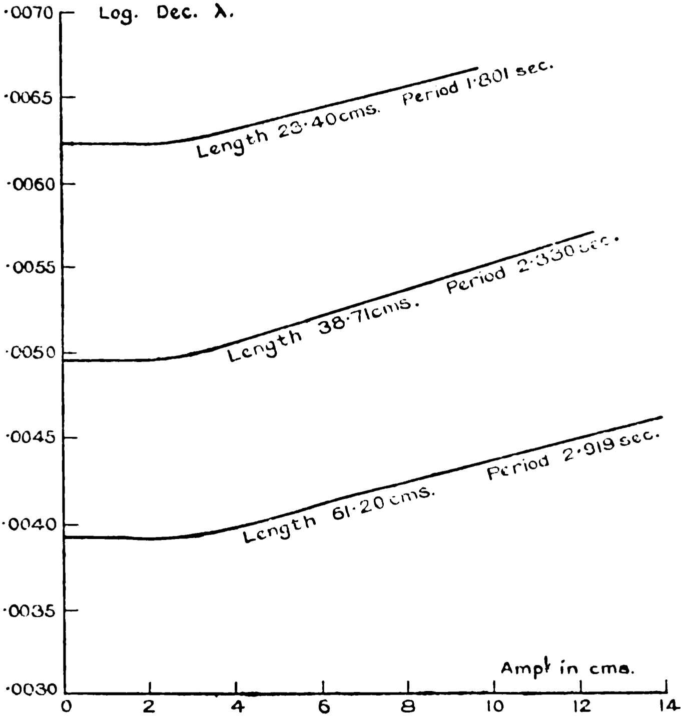


Graph 2.

Copper Wire, diam. 0·0730 cm. (Graph No. 3.)

Length, 61·20 cm. Period, 2·92 sec.		Length, 38·70 cm. Period, 2·33 sec.		Length, 23·40 cm. Period, 1·80 sec.	
Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.
13·81	0·004590	13·20	0·005746		
12·03	4484	11·81	5644		
11·50	4448	10·29	5532		
9·62	4334	9·12	5441	9·61	0·006647
8·40	4250	8·31	5374	8·30	6566
7·50	4198	7·20	5292	7·78	6537
6·17	4110	6·45	5250	7·12	6500
5·02	4048	5·50	5165	6·50	6460
4·10	3999	4·60	5100	5·31	6384
3·20	3963	4·12	5064	4·20	6320
2·81	3945	3·81	5049	3·50	6280
2·42	3941	3·20	5005	2·70	6256
1·90	3935	2·50	4962	2·18	6249
1·40	3934	2·03	4959	1·80	6246
1·01	3936	1·80	4956	1·41	6244
·831	3940	1·40	4955	·91	6245
·642	3934	1·06	4956	·71	6246
·482	3936	·818	4955	·50	6245
·301	3935	·603	4960	·28	6249
		·504	4954		
		·286	4956		

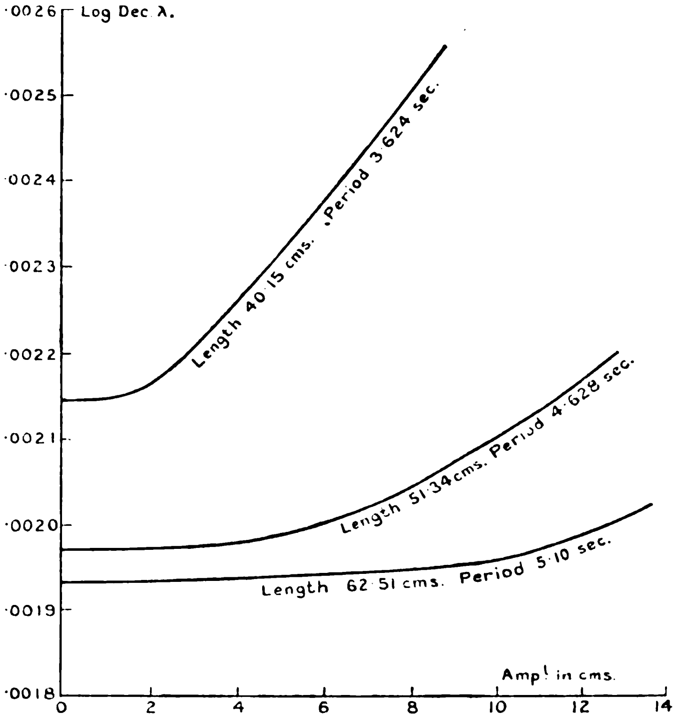
Graph 3.



Brass Wire, diam. 0·05750 cm. (Graph No. 4.)

Length, 62·50 cm. Period, 5·10 sec.		Length, 51·34 cm. Period, 4·628 sec.		Length, 40·15 cm. Period, 3·624 sec.	
Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Loc. dec.
13·50	0·002019				
12·12	1996	12·94	0 002201		
11·05	1978	11·89	2165		
10 20	1967	10·23	2106		
9·41	1959	9·40	2084		
8·73	1954	8·71	2066	8·40	0·002534
7·59	1948	7·52	2037	7·52	2474
6·23	1944	6·95	2024	6·83	2430
5·88	1942	6·00	2009	5·90	2371
5·17	1940	5·24	1997	5·01	2320
4·40	1938	4·38	1983	4·33	2281
3·90	1937	3·40	1979	3·80	2249
3·12	1935	2·89	1974	3·12	2211
2·39	1934	2·10	1972	2·80	2198
1·45	1932	1·51	1971	2·20	2169
1·00	1933	·942	1971	1·79	2158
·810	1934	·729	1970	1·24	2151
·709	1931	·602	1969	·972	2148
·602	1931	·408	1971	·799	2146
·430	1934	·283	1970	·621	2146
·291	1932			·482	2147
				·312	2144

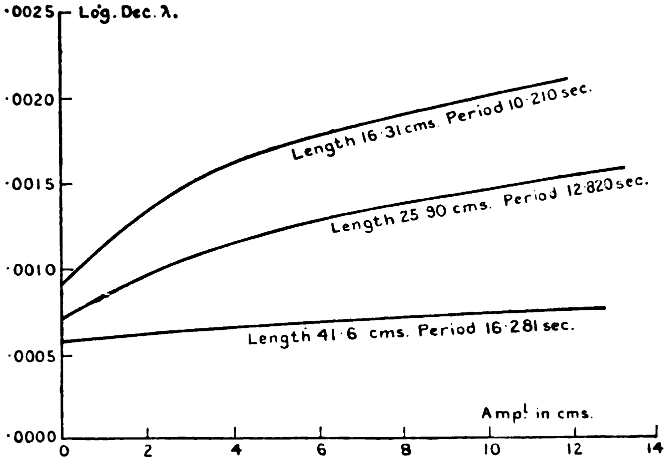
Graph 4.



Steel Piano Wire, diam. 0·02350 cm. (Graph No. 5.)

Length, 41·60 cm. Period, 16·28 sec.		Length, 25·90 cm. Period, 12·82 sec.		Length, 16·30 cm. Period, 10·21 sec.	
Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.
12·06	0·0007705	13·09	0·001626		
10·37	7532	11·80	1539	11·20	0·002088
8·97	7352	10·12	1472	10·10	2026
7·74	7218	8·24	1387	8·72	1946
6·72	7080	7·10	1325	7·15	1851
5·85	6950	6·04	1268	6·20	1785
5·12	6822	5·24	1223	5·41	1729
4·47	6732	4·83	1196	4·73	1685
3·93	6645	4·50	1170	4·20	1633
3·44	6542	3·92	1125	3·76	1594
3·04	6468	3·61	1104	3·24	1536
2·66	6415	3·23	1081	2·83	1479
2·35	6342	2·92	1046	2·49	1422
2·05	6265	2·69	1028	2·01	1349
1·82	6232	2·35	1002	1·82	1300
1·61	6185	2·10	0980	1·57	1249
1·50	6152	1·80	0949	1·11	1164
1·38	6120	1·49	0920	·931	1125
1·29	6102	1·12	0873	·802	1091
1·18	6080	·943	0847	·674	1055
·924	6022	·796	0837	·580	1045
·814	5995	·620	0821	·523	1011
·678	5960	·509	0800		

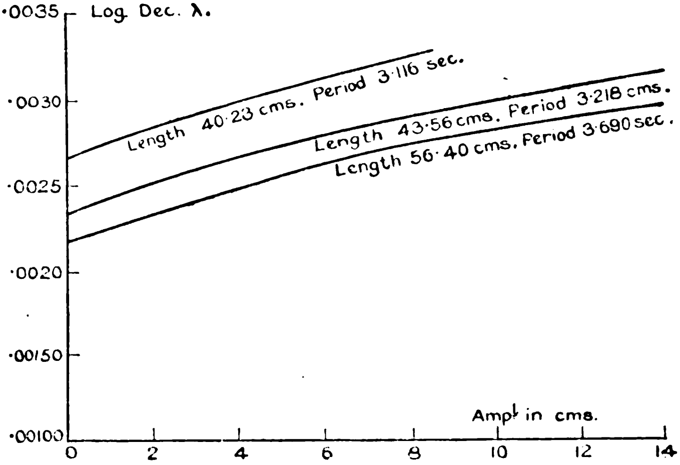
Graph 5.



Steel Piano Wire, diam. 0·05350 cm. (Graph No. 6.)

Length, 56·40 cm. Period, 3·69 sec.		Length, 43·56 cm. Period, 3·22 sec.		Length, 40·23 cm. Period, 3·12 sec.	
Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.
11·84	0·002889	13·50	0·003139		
9·60	2789	12·33	3092		
8·58	2754	11·49	3060		
7·40	2696	10·72	3019		
6·40	2642	9·80	2987		
5·22	2560	8·34	2914	8·41	0·003287
4·88	2460	7·40	2866	7·59	3210
3·75	2451	6·51	2820	6·49	3143
3·25	2400	5·72	2771	5·98	3110
2·92	2378	5·03	2725	5·10	3051
2·60	2352	4·42	2688	4·32	2999
2·28	2330	3·80	2641	3·51	2940
1·80	2296	3·01	2588	2·20	2834
1·40	2261	2·68	2563	1·70	2796
1·12	2239	2·10	2514	1·21	2756
·911	2226	1·70	2479	·852	2730
·613	2203	1·21	2430	·771	2721
·524	2192	·905	2401	·543	2703
·341	2173	·682	2384	·390	2693
·250	2169	·509	2365	·257	2679
		·392	2353	·211	2674
		·272	2340		

Graph 6.



A Study of the Results.

These values are plotted on graph paper, amplitudes in cm. being marked along the x-axis and logarithmic decrements along the y-axis. In all these experiments the scale is held at a constant distance of 74 cm., so that an amplitude of 1 cm. corresponds to a twist of $\frac{1}{74 \times 2} \times \frac{180}{\pi}$ $=0\cdot39$ of a degree. Since in no case did the amplitude exceed about 14 cm., the maximum twist to which the wires were subjected never exceeded about 4·86 degrees.

The nature of the resulting curves is indeed very suggestive, and seems to be characteristic of the particular material. With copper wires the decrement seems to be approximately constant for amplitudes *below a certain limiting value*, and then to vary linearly with it. This is the characteristic feature of one and all of the copper wires examined, and the curves suggest an equation of the form

$$\lambda_a = \lambda_0 + f(a-m),$$

where λ_a is the decrement for amplitude "a," λ_0 that when the amplitude is zero, "m" the limiting amplitude, and $f(a-m)$ a linear function. For all values of "a" less than or equal to "m," $f(a-m)=0$, so that $\lambda_a=\lambda_0$.

The value of "m" depends both on the cross-section and on the length of the wire. Owing to the dissipation of energy, the minimum decrement for a given cross-section does not correspond to the same twist per unit length of the wire. Thus, for the thinnest wire (diam. ·03302 cm.) the decrement reaches a constant value when the twist per unit length is 1·85, 1·98, and 2·13 minutes (of arc) when the lengths of the wires are 53·13, 31·93, and 26·37 cm. respectively. With the second copper wire (diam. ·0555 cm.) the constant value is reached for twists (per unit length) of 1·21, 1·02, 1·14, and 1·23 minutes when the lengths are 52·8, 34·5, 26·2, and 19·6 cm. respectively; and with the third wire (diam. ·0730 cm.) the constant value is reached for twists (per unit length) of 1·15, 1·51, and 1·84 minutes when the lengths are 61·2, 38 7, and 23·4 cm. respectively.

With wires of very narrow cross-section the curves get steeper and steeper for decreasing lengths. As the thickness of the wires is increased, it is, however, seen that they tend more and more towards parallelism. Of wires of the same material, those that are thinner appear to be steeper than those of greater cross-section.

The behaviour of brass wires is quite similar to that of copper. The logarithmic decrement remains constant over a certain range, and increases linearly thereafter. When the twists per unit length are 1·08, 1·11, and ·96 of a minute respectively, this constant value seems to have been reached. Both in the case of copper and in that of brass, as the bend of the curves is rather ill-defined, these values of twists per unit length are at best approximate. For thicker wires, however, the bend is relatively well-defined, as can be seen from the curves for copper.

The curves for steel wires, on the other hand, present features quite distinct from those of either copper or brass. The decrement does not tend to a constant value, but decreases with decreasing amplitude, more or less linearly, so that $\lambda_a = \lambda_0 + f(a)$ where $f(a)$ is a linear function. Owing to the bend of the curves, which is more pronounced with narrower than with thicker wires, the nature of this function is different according as the curve is taken before or after the bend. For wires of diameter ·02350 cm. the curves become steeper for shorter lengths, whereas with thicker steel wires they tend more towards parallelism. In the latter case the bend is less marked and the curves approximate to right lines.

Viscosities of Metals.

The equation of motion for the torsional oscillations is

$$\mathrm{I} \cdot \frac{d^2\theta}{dt^2} + b \cdot \frac{d\theta}{dt} + c\theta = 0,$$

where b and c are the damping and restoring coefficients respectively. $c = \frac{\pi \cdot n \cdot \mathrm{R}^4}{2l}$, where n is the rigidity modulus, and b, as shown by Honda (*loc. cit.*), is $\frac{\pi \cdot \eta \cdot \mathrm{R}^4}{2l}$, where η is the coefficient of viscosity. The equation thus finally becomes

$$\mathrm{I} \cdot \frac{d^2\theta}{dt^2} + \frac{\pi \cdot \eta \cdot \mathrm{R}^4}{2l} \cdot \frac{d\theta}{dt} + \frac{\pi \cdot n \cdot \mathrm{R}^4}{2l} \cdot \theta = 0,$$

the solution of which is

$$\theta = \theta_0 \cdot e^{-\frac{\pi \cdot \eta \cdot \mathrm{R}^4}{2l} \cdot \frac{t}{2\mathrm{I}}} \left(\frac{2\pi t}{\mathrm{T}} + \epsilon \right).$$

The logarithmic decrement is thus

$$\lambda = \frac{\pi . \eta . R^4 T}{8 I l};$$

$$\therefore \quad \eta = \frac{8 . I l \lambda}{\pi R^4 T}.$$

In the following tabular form the viscosities are calculated, taking the minimum values of λ :—

I, 3840·9 grm. cm.^{2} Temperature, 27°·5–29°·7 C.

Material.	R.	l.	T.	Log. dec.	$\lambda = \frac{8 I l \lambda}{\pi R^4 T} \times 10$	
	cm.	cm.	sec.	λ.	dynes per sq. cm.	
Copper	·01651	53·13	13·051	0·001046	5·610	mean 5·30
„	„	31·93	10·150	1250	5·182	
„	„	26·37	9·177	1349	5·103	
„	·02775	52·80	4·66	2614	4·888	mean 4·89
„	„	34·50	3·77	3202	4·885	
„	„	26·20	3·28	3760	4·955	
„	„	19·60	2·84	4191	4·722	
„	·03650	61·20	2·92	3935	4·550	mean 4·52
„	„	38·70	2·33	4956	4·480	
„	„	23·40	1·80	6245	4·540	
Brass	·02875	62·50	5·10	1933	3·393	mean 3·31
„	„	51·34	4·628	1970	3·129	
„	„	40·15	3·624	2146	3·404	
Steel	·01175	41·6	16·281	0582	7·635	mean 7·57
„	„	25·9	12·821	0721	7·483	
„	„	16·3	10·210	0928	7·601	
„	0·02675	56·4	3·690	2158	6·31	mean 6·30
„	..	43·56	3·218	2326	6·02	
„	„	40·23	3·116	2665	6·58	

η for a given material, though fairly constant when the cross-section is the same, appears to fall off as thickness is increased. This is true of both copper and steel.

Summary and Conclusions.

(1) The logarithmic decrement is not constant for different amplitudes, but is found to vary appreciably.

(2) In the case of copper and brass wires the decrement remains constant over a certain range, depending on the material, its length, and cross-section, and then varies linearly.

(3) The behaviour of steel wires is quite different. The decrement does not show any constant value, but falls off steadily with decreasing amplitudes.

(4) The viscosities of three different specimens of copper wire are found to be $4{\cdot}52 \times 10^8$, $4{\cdot}89 \times 10^8$, and $5{\cdot}30 \times 10^8$ dynes per sq. cm.; that of brass $3{\cdot}31 \times 10^8$ dynes per sq. cm.; and that of two specimens of steel wires $7{\cdot}57 \times 10^8$ and $6{\cdot}30 \times 10^8$ dynes per sq. cm. These discrepancies are perhaps due to varying impurities in the case of copper and to varying composition in the case of steels.

In conclusion, the authors wish to thank Prof. A. L. Narayan, M.A., D.Sc., F.Inst.P., under whose guidance the present investigation was carried out.

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LXXVI. *Internal Friction as a Cause of Shaft Whirling.*

By A. L. KIMBALL, Jr. *.

MANY articles have been written upon causes of the whirling of shafts, but, so far as the writer is aware, it is only within the last year that internal friction within the shaft, or within the rotor itself, has been suggested as a cause of whirling †.

It might be supposed, at first thought, that internal friction would damp out whirling. In this paper it will be shown that under the right conditions internal friction will sustain a whirl rather than damp it out.

Consider, for example, a shaft deflected as shown in fig. 1. Fig. 1 *a* shows a top view of a cross-section of the same shaft. Owing to its deflexion, all the fibres in the right-hand half of its cross-section are in tension T_e, and all of the fibres in the left-hand half are in compression C_e. On tending to straighten itself, the shaft reacts from right to left, or from the tension side T_e to the compression side C_e. This reaction is represented by the force vector R_e.

If internal friction exists, however, every fibre is also subject to a force due to internal friction. These internal friction forces do not depend upon the length of the fibres, but only come into play when the length of the fibres *is being changed*, such as the force resulting from the stretching of a fibre of molasses candy. When a fibre is being stretched, internal friction will evidently produce a tension; when a fibre is being compressed a compression is produced. If the shaft is revolving in a counter-clockwise direction, as indicated in fig. 1 *a*, all fibres in the lower half of the cross-section are being stretched, and are thus under frictional tension T_f, and all fibres in the upper half are being compressed, and consequently are under frictional compression C_f. Just as the *elastic* tensions and compressions on the fibres produce a reaction to the left from T_e to C_e, so also the *frictional* tensions and compressions produce a reaction upwards, in the figure, from T_f to C_f. This reaction is represented by the vector R_f.

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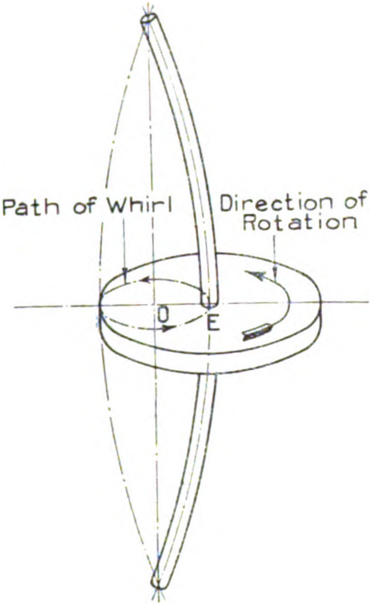
* Communicated by the Author.

† A. L. Kimball, Jr., Phys. Review, xxi. p. 703 (June 1923). B. L. Newkirk, G. E. Review, xxvii. p. 169 (March 1924). A. L. Kimball, Jr., G. E. Review, xxvii. p. 244 (April 1924).

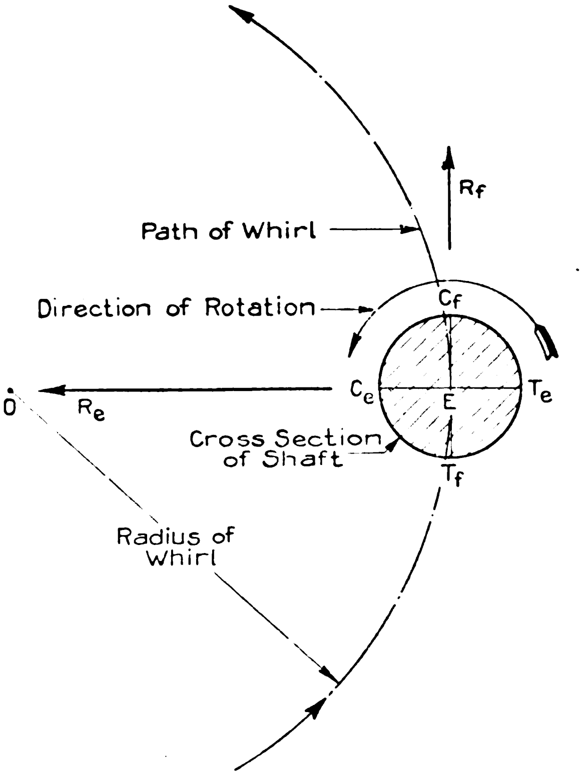
Fig. 1.



The elastic reaction R_e may be very powerful, and will quickly disappear unless maintained by centrifugal force when the entire shaft and fly-wheel are "whirling" at or very close to the critical resonant speed. The frictional reaction R_f, although far smaller than R_e, is seen to be unbalanced, so that as long as R_f is in the same direction as the whirl, as shown in fig. 1, the whirl must continually build up until frictional resistance is produced sufficient to balance the disturbing force R_f.

The disturbing force R_f is in the same direction as the whirling motion in the case cited, so that whirling builds up. A further consideration of fig. 1 *a* shows that this is only true when the shaft rotates about E faster than the plane of

Fig. 1 *a*.



deflexion of the shaft revolves about O, otherwise the fibres shown in the upper half of the cross-section given in the figure will be increasing instead of decreasing in length, and those below will be decreasing instead of increasing in length, causing the reaction R_f due to frictional forces to reverse, and to act against the motion of the shaft in its path of whirl instead of with this motion. Whirling will be damped out instead of sustained, due to this cause when the shaft is revolving more slowly than its natural whirling speed.

In order to build up a whirl from internal friction action, therefore, a shaft must revolve with a higher speed than its whirling speed. Furthermore, it is seen that, due to internal friction, a shaft may whirl when running at any speed of revolution above its critical speed. The whirling itself must be at or near the critical speed. A whirl at any other speed is dynamically impossible without a powerful disturbing force, just as the vibration of a reed at any other than its natural frequency is impossible without a strong stimulus.

Fortunately, in steel such as is used for ordinary shafting the internal friction is so small that a whirl, due to this cause, will not develop unless the conditions are exactly right. For example, if the bearings are not rigidly supported, the energy loss because of their vibration may completely annul the effect.

It has been discovered that this internal friction action may be greatly increased if a shaft has external parts such as rings shrunk on to it. In such a case a whirl is very difficult to avoid. The disturbing force R_f (fig. 1 *a*) is caused just as before, except that the friction comes largely from the rubbing of the surface fibres of the shaft against the inner surface of the ring, which is shrunk on to the shaft. This surface friction may be so great as to cause a shaft to take a slight permanent set when given a small deflexion. Under these conditions a whirl is almost certain to develop when the rotational speed rises above the critical speed.

This cause of whirling was discovered in connexion with a peculiar whirling or whipping developed by large turbo compressors built by the General Electric Company of America [*], and has been overcome chiefly by the use of spring bearings producing an absorption of vibrational energy.

In this article no assumptions are made as to what laws the internal frictional force obeys, as they are not well understood. The important fact is that this disturbing force must exist if internal friction is present, and that the force may produce whirling.

Research Laboratory,
General Electric Company,
Schenectady, N.Y.
July 25, 1924.

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[*] B. L. Newkirk, Gen. Elec. Review, xxvii. p. 169 (March 1924).

LXXVII. *A Class of equivalent Electrical Networks.* *By* The Research Staff of the General Electric Co., Ltd.* (*Work conducted by* A. C. BARTLETT.)

Summary.

FIRSTLY, it is shown that there exists a large number of alternative networks that have the same impedance as networks made up of numbers of T, II. or Bridge artificial line sections short-circuited or open-circuited at the far end.

Secondly, by the use of these networks a single Bridge type section can be made in a large number of ways that is equivalent, both as regards input and output terminals, to an artificial line consisting of any number of equal sections.

A Class of equivalent Electrical Networks.

IN telephone engineering use is often made of artificial lines composed of a number of similar sections, each section having two input terminals and two output terminals, the input terminals of any section being connected to the output terminals of the previous section. The most common sections are the T, II, and Bridge sections shown in figs. 1, 2, and 3, the impedance elements A & B being each composed

Fig. 1.

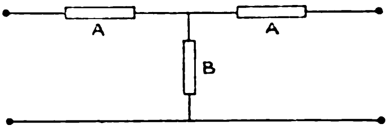
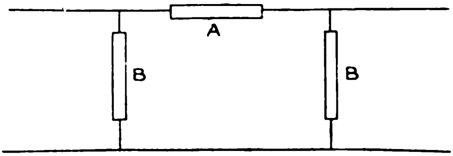


Fig. 2.



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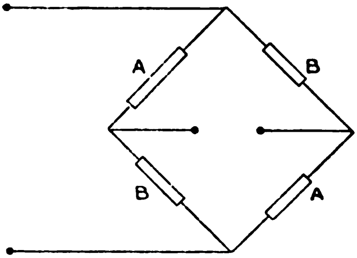
* Communicated by the Director.

of some arrangement of resistances, condensers, and inductances. Electric wave filters are a special case in which A & B are pure reactances.

Fig. 3.



The general transmission theory of such networks is identical with that of the uniform line except that n, the number of sections, replaces l the length of the uniform line.

Whichever form of section is employed the impedance of n sections is $Z_0 \tanh n\theta$ if the network is short-circuited at the far end, and $Z_0 \coth n\theta$ if it is open at the far end, where Z_0 is the characteristic impedance, and θ the propagation constant of a single section. The relations between Z_0 and θ for the different sections are given below.

T section.

$$Z_0 = \sqrt{A^2+2AB},$$

$$Z_0 \tanh \frac{\theta}{2} = A,$$

$$Z_0/\sinh \theta = B,$$

$$Z_0 \coth \frac{\theta}{2} = A+2B,$$

$$Z_0 \tanh \theta = A + \frac{AB}{A+B},$$

$$Z_0 \coth \theta = A+B.$$

Π section.

$$Z_0 = \frac{AB}{\sqrt{A^2 + 2AB}},$$

$$Z_0 \sinh \theta = A,$$

$$Z_0 \coth \frac{\theta}{2} = B,$$

$$Z_0 \tanh \frac{\theta}{2} = \frac{1}{\frac{1}{B} + \frac{2}{A}} = \frac{A^2 B}{A^2 + 2AB},$$

$$Z_0 \tanh \theta = \frac{1}{\frac{1}{B} + \frac{1}{A}} = \frac{AB}{A+B},$$

$$Z_0 \coth \theta = \frac{1}{\frac{1}{B} + \frac{1}{A+B}} = \frac{B(A+B)}{A+2B}.$$

Bridge section.

$$Z_0 = \sqrt{AB},$$

$$Z_0 \coth \frac{\theta}{2} = A \text{ or } B,$$

$$Z_0 \tanh \frac{\theta}{2} = B \text{ or } A.$$

Of course only two equations are independent in each case: the reason for giving more than two will appear later. In this paper it will be shown firstly, that there is a large number of networks that have the same impedance at all frequencies as an artificial line consisting of any number of either similar T, Π, or Bridge sections open or short circuited at the far end; and secondly, that a single Bridge type section can be constructed that is equivalent at all frequencies, both as regards input and output terminals, to an artificial line consisting of any number of either T, II, or Bridge sections.

Considering the first part of the problem. Any expansion of $Z \tanh n\theta$ or $Z \coth n\theta$ in terms of simpler functions, such as $Z_0 \tanh \theta$, $Z_0 \coth \theta$, or $Z_0 \sinh \theta$, that represents the impedance of a network built up of the simple networks represented by these functions will give a network whose impedance is $Z_0 \tanh n\theta$ or $Z_0 \coth n\theta$.

Examination of hyperbolic identities show that a large number exist that fulfil these conditions.

Among the most important are :—

$$\operatorname{Tanh} n\theta = \frac{n\tanh\theta}{1+}\,\frac{(n^2-1^2)\tanh^2\theta}{3+}\,\frac{(n^2-2^2)\tanh^2\theta}{5+}\cdots,$$

$$\operatorname{Tanh} n\theta = \sum_{r=0}^{r=\frac{n}{2}-1} \frac{\tanh\theta\,.\,\dfrac{2}{n\sin^2\dfrac{2r+1}{2n}\,.\,\pi}}{1+\dfrac{\tanh^2\theta}{\tan^2\dfrac{2r+1}{2n}\,.\,\pi}}$$

when n is even,

$$\operatorname{Tanh} n\theta = \frac{\tanh\theta}{n} + \sum_{r=0}^{r=\frac{n-3}{2}} \frac{\tanh\theta\,.\,\dfrac{2}{n\sin^2\dfrac{2r+1}{2n}\,.\,\pi}}{1+\dfrac{\tanh^2\theta}{\tan^2\dfrac{2r+1}{2n}\,.\,\pi}}$$

when n is odd,

$$\operatorname{Coth} n\theta = \frac{1}{n}(\tanh\theta+\coth\theta) + \sum_{r=1}^{r=\frac{n}{2}-1} \frac{\tanh\theta\,.\,\dfrac{2}{n\sin^2\dfrac{r\pi}{n}}}{1+\dfrac{\tanh^2\theta}{\tan^2\dfrac{r\pi}{n}}}$$

when n is even,

$$\operatorname{Coth} n\theta = \frac{\coth\theta}{n} + \sum_{r=1}^{r=\frac{n-1}{2}} \frac{\tanh\theta\,.\,\dfrac{2}{n\sin^2\dfrac{r\pi}{n}}}{1+\dfrac{\tanh^2\theta}{\tan^2\dfrac{r\pi}{n}}}$$

when n is odd,

$$\operatorname{Tanh}\frac{n\theta}{2} = \frac{1}{n}\sum_{r=0}^{r=\frac{n}{2}-1} \frac{1}{\dfrac{\sin^2\dfrac{2r+1}{2n}\,.\,\pi}{\sinh\theta}+\frac{1}{2}\tanh\dfrac{\theta}{2}}$$

when n is even,

$$\operatorname{Coth}\frac{n\theta}{2}=\frac{1}{n}\left\{2\coth\theta+\sum_{r=1}^{r=\frac{n}{2}-1}\frac{1}{\dfrac{\sin^2\dfrac{r\pi}{n}}{\sinh\theta}+\frac{1}{2}\tanh\dfrac{\theta}{2}}\right\}$$

when n is even.

$$\operatorname{Tanh}\frac{n\theta}{2}=\frac{1}{n}\left\{\tanh\frac{\theta}{2}+\sum_{r=0}^{r=\frac{n-3}{2}}\frac{1}{\dfrac{\sin^2\dfrac{2r+1}{2n}\,.\,\pi}{\sinh\theta}+\frac{1}{2}\tanh\dfrac{\theta}{2}}\right\}$$

when n is odd,

$$\operatorname{Coth}\frac{n\theta}{2}=\frac{1}{n}\left\{\coth\frac{\theta}{2}+\sum_{r=1}^{r=\frac{n-1}{2}}\frac{1}{\dfrac{\sin^2\dfrac{r\pi}{n}}{\sinh\theta}+\frac{1}{2}\tanh\dfrac{\theta}{2}}\right\}$$

when n is odd.

First, consider the identity

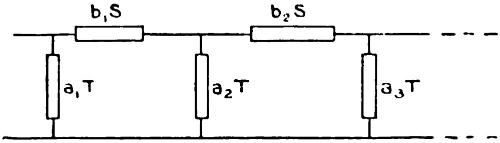
$$\tanh n\theta=\frac{n\tanh\theta}{1+}\;\frac{(n^2-1^2)\tanh^2\theta}{3+}\;\frac{(n^2-2^2)\tanh^2\theta}{5+}\cdots$$

From this we obtain

$$Z_0\tanh n\theta=\frac{1}{1/nZ_0\tanh\theta+}\;\frac{1}{\dfrac{3n}{n^2-1^2}\,.\,Z_0\coth\theta+}\;\frac{1}{1\Big/\dfrac{n(n^2-2^2)}{5(n^2-1^2)}\,.\,Z_0\tanh\theta+}\cdots$$

But this is the impedance of the network of fig. 4:

Fig. 4.



where
$$S = Z_0 \coth\theta,$$
$$T = Z_0 \tanh\theta,$$

$$a_1 = n, \qquad b_1 = \frac{3n}{n^2-1},$$

$$a_2 = \frac{n(n^2-2^2)}{5(n^2-1)}, \qquad b_2 = \frac{7n(n^2-2^2)}{(n^2-1)(n^2-3^2)}$$

$$a_3 = \frac{n(n^2-2^2)(n^2-4^2)}{9(n^2-1^2)(n^2-3^2)}, \qquad b_3 = \frac{11n(n^2-2^2)(n^2-4^2)}{(n^2-1)(n^2-3^2)(n^2-5^2)}.$$

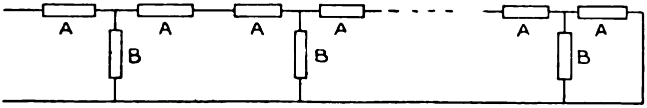
Consider for example the T section artificial line:

$$Z_0 \coth\theta = A + B.$$

$$Z_0 \tanh\theta = A + \frac{AB}{A+B} = A + \frac{1}{\frac{1}{A}+\frac{1}{B}}.$$

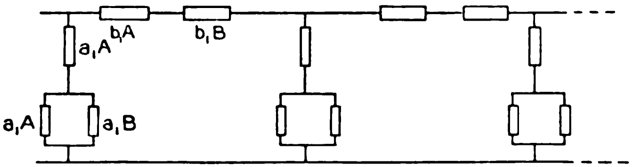
Then $Z_0 \tanh n\theta$, which is the impedance of the network of fig. 5 having n sections, and short-circuited at the far end,

Fig. 5.



is by the above result shown to be also the impedance of the network of fig. 6.

Fig. 6.



A like result for $Z_0 \coth n\theta$ can be obtained from the same expansion of $\tanh n\theta$ but can be written down directly by means of the Method of Reciprocal Impedances, which may be regarded as a special case of the Principle of Duality *

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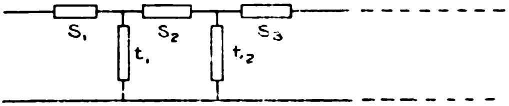
* Russell, 'Alternating Currents,' vol. i. chap. xxi.

and may be briefly stated as follows:—

Let P and Q be two impedances, then $\frac{P^2}{Q}$ will be an impedance, and may be termed the reciprocal of Q with respect to P.

Consider any network of the ladder type as fig. 7 having an impedance X, [illegible]

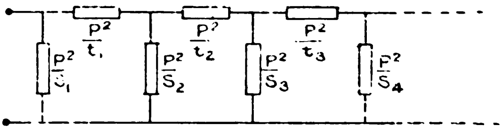
Fig. 7.



and consisting of a number of series elements S_1, S_2, S_3, etc. and shunt elements t_1, t_2, t_3, etc.

Construct a network having shunt elements $\frac{P^2}{S_1}$, $\frac{P^2}{S_2}$, $\frac{P^2}{S_3}$, and series elements $\frac{P^2}{t_1}$, $\frac{P^2}{t_2}$, $\frac{P^2}{t_3}$, as in fig. 8:

Fig. 8.



and let its impedance be Y. Then it can easily be shown that

$$Y = \frac{P^2}{X},$$

i. e. Y is the reciprocal of X with respect to P.

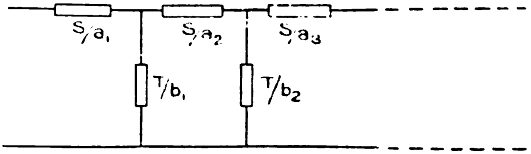
Returning to the case of $Z_0 \coth n\theta$.

$$Z_0 \coth n\theta = Z_0^2/Z_0 \tanh n\theta,$$

and is thus the reciprocal of $Z_0 \tanh n\theta$ with respect to Z_0.

Therefore we can write down a network for $Z_0 \coth n\theta$ by reciprocating the network of fig. 4 with respect to Z_0, obtaining the result of fig. 9:

Fig. 9.



where S, T, a_1, a_2, etc. and b_1, b_2, etc. have the same meaning as in fig. 4. From these networks others can be derived by replacing θ by $\left(\theta + j\frac{\pi}{2}\right)$; this substitution changes $\coth\theta$ to $\tanh\theta$, and vice versa; if n is even, $\coth n\theta$ and $\tanh n\theta$ remain unchanged; if n is odd, $\coth n\theta$ is changed to $\tanh n\theta$, and vice versa. Thus in the networks of figs. 4 and 9, if n is even the interchange of $\tanh\theta$ and $\coth\theta$ throughout the network does not change its value, whereas if n is odd, the interchange changes the impedance of the network from $Z_0 \tanh n\theta$ to $Z_0 \coth n\theta$, and vice versa.

Taking the identity,

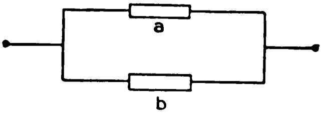
$$Z_0 \tanh n\theta$$

$$= \Sigma \frac{Z_0 \tanh\theta \dfrac{2}{n \sin^2 \dfrac{2r+1}{2n}.\pi}}{1 + \dfrac{\tanh^2\theta}{\tan^2 \dfrac{2r+1}{2n}.\pi}}$$

$$= \Sigma \frac{1}{\dfrac{1}{Z_0 \tanh\theta . \dfrac{2}{n \sin^2 \dfrac{2r+1}{2n}.\pi}} + \dfrac{1}{Z_0 \coth\theta . \dfrac{2}{n \cos^2 \dfrac{2r+1}{2n}.\pi}}}.$$

Now the expression under the Σ is the impedance of the network of fig. 10:

Fig. 10.



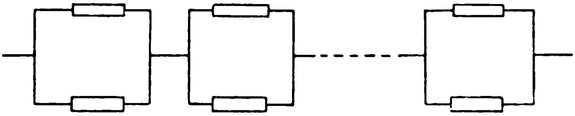
where

$$a = Z_0 \coth\theta . \frac{2}{n \cos^2 \dfrac{2r+1}{2n}.\pi},$$

$$b = Z_0 \tanh\theta . \frac{2}{n \sin^2 \dfrac{2r+1}{2n}.\pi}.$$

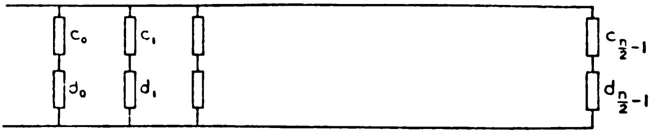
Thus $Z_0 \tanh n\theta$ is the impedance of the network fig. 11:

Fig. 11.



consisting of $\frac{n}{2}$ elements as fig. 10 connected in series. Reciprocating with respect to Z_0, we have $Z_0 \coth n\theta$ as the impedance of the network of fig. 12:

Fig. 12.



consisting of $\frac{n}{2}$ shunt elements,

where $$c_r = Z_0 \tanh\theta \,.\, \frac{n}{2} \cos^2 \frac{2r+1}{2n} \,.\, \pi$$

and $$d_r = Z_0 \coth\theta \,.\, \frac{n}{2} \,.\, \sin^2 \frac{2r+1}{2n} \,.\, \pi.$$

Taking the expansion,

$$Z_0 \coth n\theta = \frac{Z_0}{n}(\tanh\theta + \coth\theta) + \sum_{r=1}^{r=\frac{n}{2}-1} \frac{Z_0 \tanh\theta \,.\, \dfrac{2}{n \sin^2 \dfrac{r\pi}{n}}}{1 + \dfrac{\tanh^2\theta}{\tan^2 \dfrac{r\pi}{n}}},$$

in the same way $Z_0 \coth n\theta$ is the impedance of a network of the form of fig. 11.

Reciprocating with respect to Z_0:

$Z_0 \tanh n\theta$ is the impedance of a network of the form fig. 12.

Results of similar form follow when n is odd.

Thus it will be seen that both $Z_0 \tanh n\theta$ and $Z_0 \coth n\theta$ can be represented by alternative networks either of the form of a ladder network or a number of simple impedances connected either in series or in parallel.

It will be seen that these results are analogues of results previously given for the uniform line*. Both in the case of the artificial and of the uniform line the equivalent networks for $Z_0 \tanh n\theta$, $Z_0 \coth n\theta$, $Z_0 \tanh Pl$, and $Z_0 \coth Pl$ that take the form of a number of simple networks connected in parallel may be regarded as statements in physical form of the corresponding Heaviside expansion for the input current.

From these results many other networks for $Z_0 \tanh n\theta$ and $Z_0 \coth n\theta$ can be derived.

$Z_0 \tanh \frac{\theta}{2}$ and $Z_0 \coth \frac{\theta}{2}$ are physically realizable, hence we can expand in terms of $\frac{\theta}{2}$; if n has a factor n_1, we can expand $\tanh n\theta$ in terms of $n_1\theta$, and we can also write

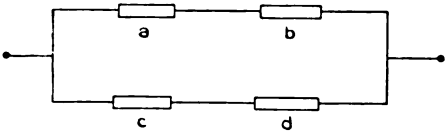
$$Z_0 \tanh n\theta$$

$$= Z_0 \tanh \{(n-r)\theta + r\theta\}$$

$$= 1 \Big/ \left\{ \frac{1}{Z_0 \coth (n-r)\theta + Z_0 \tanh r\theta} + \frac{1}{Z_0 \tanh (n-r)\theta + Z_0 \coth r\theta} \right\},$$

which is the impedance of the network fig. 13:

Fig. 13.



where

$$a = Z_0 \coth (n-r)\theta,$$
$$b = Z_0 \tanh r\theta,$$
$$c = Z_0 \coth r\theta,$$
$$d = Z_0 \tanh (n-r)\theta,$$

and expand the elements of this network.

The second result, namely the formation of a single Bridge type equivalent to any number of T, Π, or Bridge sections follows from a consideration of the relations between the propagation constant and characteristic impedance of the Bridge section and its impedance elements.

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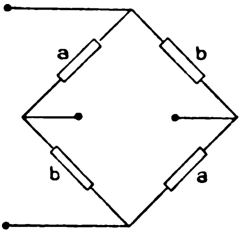
* Phil. Mag. Nov. 1924.

Consider a Bridge type section, fig. 14:

Fig. 14.



where $$a = Z_0 \tanh \frac{n\theta}{2},$$

$$b = Z_0 \coth \frac{n\theta}{2},$$

its line characteristic impedance is Z_0 and its propagation constant is $n\theta$.

Thus, as regards both output and input terminals it will exactly replace an artificial line consisting of n sections such as fig. 3.

Now if n is even, $Z_0 \coth \frac{n\theta}{2}$ and $Z_0 \tanh \frac{n\theta}{2}$ are the impedances of $\frac{n}{2}$ Bridge sections of fig. 3 open or short circuited at the far end respectively; and if n is odd, the impedances are those of $\frac{n-1}{2}$ Bridge sections of fig. 3 closed through $Z_0 \tanh \frac{\theta}{2}$ or $Z_0 \coth \frac{\theta}{2}$ at the far end respectively. Further, from the previous sections we know that if $Z_0 \tanh \frac{\theta}{2}$ and $Z_0 \coth \frac{\theta}{2}$ are physically realizable, we can form other networks having impedances $Z_0 \coth \frac{n\theta}{2}$ and $Z_0 \tanh \frac{n\theta}{2}$.

Thus, given any Bridge type of artificial line consisting of any number of sections, we can construct a single Bridge type section that will replace it identically as regards both input and output terminals, and this can be done in a large number of ways.

Now returning to Π and T sections, in both cases $Z_0 \coth\frac{\theta}{2}$ and $Z_0 \tanh\frac{\theta}{2}$ are physically realizable, as also are $Z_0 \tanh\frac{n\theta}{2}$ and $Z_0 \coth\frac{n\theta}{2}\Big)$. Thus we can construct a single Bridge type section, and this in a large number of ways, equivalent to any number of given Π or T sections.

LXXVIII. *Ultimate Rational Units and Dimensional Theory.*

By Prof. GILBERT N. LEWIS, *Ph.D.*[*]

THERE have appeared recently several criticisms of the theory of ultimate rational units which demand reply. When my recent paper appeared in the Philosophical Magazine[†], one of the editors (O. J. L.) felt impelled to protest against the theory of ultimate rational units in a note appended to my article. However, since there is nothing in this note with which I cannot fully agree, one of us must misunderstand the other.

Next, Dr. Norman Campbell[‡] has, in a highly provocative paper, attacked the theory of ultimate rational units. He begins by saying: "'O. J. L.,' in appending to this last paper some general objections to Prof. Lewis's arguments (in which I concur entirely), has omitted to draw attention to the simple reasoning whereby it can be demonstrated to be false." This reasoning will be analyzed presently. Meanwhile it is to be noted that Dr. Campbell himself appears dissatisfied with his formal proof, and proceeds to a psychoanalytical investigation of my motives in propounding the theory, and of Planck's motives in not refuting it[§], and he ends by stating that the theory of ultimate rational units may prove true, but, if so, that it will be useless, which seems incompatible with the statement that it is "demonstrably false." Nevertheless, when allowance is made for the vivid forensic style of Dr. Campbell, I find that I can agree with the greater part of what he writes (except always where he purports to state my own views), and, again, we must inquire what deep-seated misunderstanding on the one side or the other has provoked so heated a polemic.

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[*] Communicated by the Author.

[†] Phil. Mag. xlv. p. 266 (1923).

[‡] Phil. Mag. xlvii. p. 159 (1924).

[§] Dr. Campbell gathers "from Planck's exposition of that subject that he judged the errors which have led Prof. Lewis astray too obvious to be worth noticing explicitly."

Finally, I shall refer to a criticism contained in the very stimulating little book of Bridgman on "Dimensional Analysis"[*]. Here he states, referring to one of the consequences of U.R.U., "It is undeniable that the result is of such simplicity that it seems probable that the coefficient may be the result of a mathematical process, and is not merely due to a chance combination of elements in a dimensionally correct form," but adds, "The justification of this point of view (theory of U.R.U.) at present is not to be found in any accurate results of measurement, but is rather quasi-mystical in its character." In the course of this article we shall find occasion to examine this question and attempt to ascertain just what is the quasi-mystical element that enters into the new theory.

In examining these various criticisms, it has seemed to me that the source of the feelings of opposition engendered by the statement of the theory of U.R.U. springs from certain prevailing ideas concerning the dimensions of physical quantities, and it seems therefore desirable to show once more, as Dr. Adams and I did in our original article[†], that the theory of ultimate rational units may be presented without any statement or implication concerning dimensions.

The Simplest Statement of the Theory of Ultimate Rational Units.

Admitting that the centimetre, the gram, the second, and the degree are units which possess no profound theoretical significance, it is legitimate and desirable to inquire whether new sets of units may not be invented which will lead to a simplification of the equations of physics. Such an attempt was made by Planck, who employed for the fixing of his new units four experimental constants of universal importance—namely, the velocity of light c, the Boltzmann constant k (gas constant for one molecule), the Planck constant h, and the constant of gravitation f. His method consisted merely in finding units of mass, length, time, and temperature which would make each of these constants *numerically* equal to unity. The first two steps taken by Planck were also taken by Adams and myself, and I doubt if anyone familiar with the present state of physical science, and willing to attempt the reform of the system of units, would do otherwise than eliminate first of all the k which is affixed to temperature T in every fundamental equation of kinetic theory and of thermal radiation, and the c which accompanies the time t in all of the equations of electromagnetism and of relativity.

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[*] Yale University Press, 1922.

[†] Phys. Rev. iii. p. 92 (1914).

Our third step departs from Planck's procedure and makes use of the charge upon an electron *. Now, no one will question that this charge, which is that of a singly-charged ion, positive or negative, is a quantity of really fundamental significance. Nevertheless, if we decide to make this quantity the unit of electric charge, it still remains to define unit charge in terms of units of length, time, and mass before we can take the third step toward the reform of our present units. The dilemma may be illustrated by considering the third step of Planck's procedure. In certain fields of quantum theory the constant h seems no more fundamental than the constant $h/2\pi$, but if Planck had decided to make the latter constant numerically equal to unity, he would have arrived at an entirely different set of units. A similar ambiguity arose in connexion with the third step of our procedure, since two systems of electrostatic units were already in vogue. If e represents the charge upon an electron in ordinary electrostatic units, the same charge in Heavyside electrostatic units becomes $(4\pi)^{\frac{1}{2}}e$. Which of these two numerical values should be placed equal to unity? In fact, we chose neither of these, but rather the value $4\pi e$. In other words, we chose $(4\pi e)^2$ to be our new unit of energy × length. We admitted that this decision, which seems arbitrary, was reached after looking ahead to some of its consequences. But even if the decision should appear to be purely arbitrary, it is a perfectly legitimate attempt to improve our existing set of units.

The fourth step corresponding to Planck's use of the constant of gravitation we have not yet taken, so that for the present we are content to employ any set of units which makes c, k, and $4\pi e$ numerically equal to unity. For example, we may preserve provisionally the centimetre as the unit of length, and thus determine the three new units of mass, time, and temperature. With such a set of units we stated, as our new theory, that if such a system of units be

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* Dr. Campbell devotes much space to proving the somewhat elementary proposition that it is not always possible to define n units by means of n constants. Thus it would be impossible to define units of mass, length, and time by means of the three constants c, h, and e (electron charge). He does not claim, however, that we have used such a set of constants, and his remarks do not seem therefore pertinent to the present discussion.

employed, "then all universal constants will prove to be pure numbers, involving only integral numbers and π." Our first application of this theory was to the constant of Stefan's law, and we asserted that this constant (radiant energy per unit volume at unit temperature) is numerically equal to unity when energy, volume, and temperature are expressed in our new units. This assertion was in agreement with experimental determinations of Stefan's constant within the wide limits of experimental error which at that time existed.

The whole proof of the demonstrable falsity of the theory of ultimate rational units brought forward by Dr. Campbell is that, no matter how narrow the experimental limits of error may be, there always remains within these limits an infinite number of values consistent with the experiments. But this is not a disproof of the theory of ultimate rational units, but rather a statement that from a purely logical standpoint no proof of any physical theory can ever be obtained. If, however, we predict from our theory certain numerical values, and if with continual refinement of experimental technique the experimental results come nearer and nearer to the predicted value, this will come as near to a proof of the theory as most scientists demand.

We predicted that the constant σ of Stefan's law would be $5{\cdot}70 \times 10^{-5}$. From this, assuming Planck's radiation law to be either a true relation or a very close approximation to the truth, we predicted that the Planck constant h would prove to be $6{\cdot}560 \times 10^{-27}$. In the second volume of Planck's 'Wärmestrahlung,' which appeared at the same time as our paper, he gave $\sigma = 5{\cdot}54 \times 10^{-5}$ and $h = 6{\cdot}415 \times 10^{-27}$ as the best experimental values then obtainable. The present accepted experimental values are $\sigma = 5{\cdot}72 \times 10^{-5}$ and $h = 6{\cdot}554 \times 10^{-27}$. Hence I stated in my recent paper that "unless, therefore, we are to assume a bizarre coincidence, the recent determinations of the constants of Stefan and Planck furnish a striking justification of the ideas which Dr. Adams and I advanced." If further and better measurements of Stefan's constant lead to values nearer to the one predicted, we should be justified in considering the theory of ultimate rational units as proved for this one instance at least.

The second application of the theory of ultimate rational units concerned the universal constant which appears in the entropy equation of a monatomic gas. Here, also, I predicted that the expression for the entropy per molecule would prove to be numerically equal to unity after expressing all the quantities involved in ultimate rational units[*]. This I have shown to be in remarkably good agreement with existing experimental data, and I predict that the agreement will become still better as the measurements are improved.

What is a Simple Number?

In my more recent formulation of the theory I have stated that any universal constant would, in terms of U.R.U., prove to be a simple number, and the question of how we may logically define a "simple number" has greatly troubled both Professor Bridgman and Dr. Campbell. Perhaps it would have been better if I had adhered to the more guarded statement given in our first paper which I have just quoted, but it seemed to me that such criticism would be to some extent disarmed by the fact that in the two cases where an unqualified prediction has been made, namely, for the constants of black-body radiation and of the entropy of the non-atomic gas, the number used was in each case unity, which would in general I presume be regarded as a simple number. In any case the simplicity of the number assigned to any universal constant would necessarily be relative to the physical conditions which are imposed. Thus, if in defining Stefan's constant we consider the energy radiated per second from a black watch-spring of given size and shape, we should again find the energy radiated to be proportional to the fourth power of the temperature, but the constant of proportionality would be a very complicated number owing to the shape of the spring. If, however, we eliminate such complications in so far as we can foresee them, we may expect our universal constants to be as simple numbers as those which appear, for example, in a short table of definite integrals. The concrete question which has been raised concerns the Planck radiation formula, which by direct integration gives (in U.R.U.) $ah^3 = \frac{8\pi^5}{15}$, where a is Stefan's constant and h is Planck's. If $a=1$ we obtain h as a rather complicated number. Is this consistent with our theory as stated? I cannot answer this question in any positive way, but from the fundamental character of the quantities involved, and from the lack of any obvious complicating "shape-factors" and the like, it is my belief that the constant *h* will prove to be a much simpler number than the one thus obtained, and therefore that Planck's radiation formula will prove to be only an extremely close approximation to the true radiation formula.

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[*] It seems that part of Dr. Campbell's objections to U.R.U. is due to his having made some simple mistake whereby he concludes that my value for the constant of the entropy equation is $N^{5.2}$ instead of unity, where N is the Avogadro number. It is perhaps not surprising, therefore, that he considers the theory fantastic.

It is to be noted in this connexion that Bridgman, while criticizing the concept of a simple number, adopts and employs an idea of Einstein *, namely, that a suspected physical relation obtained by considerations of dimensionality becomes probable if the numerical coefficients involved are found to be small numbers. It might, however, be difficult to explain just what is to be meant by a small number.

Is there a Mystical Element in the Theory?

I think that every scientist at some time makes use of a vague principle which may be expressed as a belief in the simplicity of natural laws. This belief we may call mystical since we have not the slightest idea whether its undoubted usefulness is due to the structure of the objective world, or to some hitherto unanalyzed trait of human psychology. The theory of ultimate rational units was based consciously upon this belief, and therefore Bridgman is perhaps justified in calling it quasi-mystical. All that I desire to point out here is that every physicist employs the same principle in other but quite analogous ways.

When the change of the mass of an electron with its velocity was first being studied, there were two rival theories, one of Abraham and one of Lorentz. However, the equation obtained by Abraham was so complicated that it seemed unlikely that it could be an exact expression for so simple a phenomenon, although the first experiments seemed to favour it. No one now doubts the accuracy of the very simple equation which was advanced by Lorentz.

Since, however, this illustration may appeal only to a limited number, let us consider some far more familiar applications of the principle of simplicity. When Stefan proposed a purely empirical equation † for the emission of radiant energy from a black body, he introduced 4 as the exponent of temperature in that equation, which agreed with observations within the limits of experimental error; but, as Dr. Campbell would say, "so also would infinitely many other values." Again, let us consider Newton's law of gravitation. Neither the observations which had been made in Newton's time nor the more accurate ones which have since been obtained would enable us to say that the exponent of the distance in the gravitation equation is exactly 2 and not some number which differs by a minute amount* from 2. If we find deviations from Newton's law our instinct is not to make a slight change in the exponent, but rather to invent some entirely new functional relationship which may reduce to the inverse square law in the limit.

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* *Ann. Phys.* xxxv. p. 679 (1917).

† The exactness of this equation was later proved thermodynamically by Boltzmann. Many such examples of experimental equations which have later been theoretically deduced tend to confirm our belief in the principle of simplicity.

The fact that all the equations of physics which are regarded as at all fundamental contain exponents which involve only integers or simple fractions, is a striking example of the universal belief in the essential simplicity of natural laws.

Instead of writing the laws of Stefan and of Newton in their complete form, let us write

$$\frac{E}{V}=aT^p; \quad F=f\frac{m_1m_2}{r^q}.$$

The theory of ultimate rational units states that the same "mystical" principle which leads us to expect the exponents of such quantities as T, r, and m_1 to be simple numbers, leads also to the expectation that the coefficients a and f will appear as simple numbers, when such units as are based on the circumference of the earth and the density of water are eliminated.

The Dimensions of Physical Quantities.

All that is essential to the theory of ultimate rational units can be stated without any reference to the physical dimensions of the magnitudes considered. It is perhaps unfortunate therefore that in my recent exposition of this theory I superimposed upon it certain considerations which introduced so controversial a subject as the theory of dimensionality; for while I consider that such considerations are valuable, they seem to be almost solely responsible for the opposition which my paper has aroused. There is a taint of heresy attached to any suggested modification of the

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[*] It is true that some authors have proposed a different exponent of r in the gravitation equation: for example, 2·0000002. If such an equation were to be adopted it would be interesting to inquire into the dimensions of the constant of gravitation.

orthodox statements regarding fundamental and derived magnitudes. Dr. Campbell challenges me to an admission of heresy by propounding the following dilemma :—"Either the statement that such a derived magnitude (*e. g.* velocity) has the conventional dimensions (*e. g.* lt^{-1}) is the expression of some scientific law or fact; or it is not." . . . . "If it is not such an expression, but is a mere convention, then it is impossible to deduce from it anything scientifically significant, whether true or not." I have no fault to find with this statement, although he has chosen a magnitude which has never so far been defined otherwise than dl/dt. But referring to derived units in general, I do emphatically assert that the dimensions which they are assigned are the result of mere conventions (although these conventions are extremely useful), and it is impossible to deduce anything scientifically significant from the assumption that these dimensions are inherent in the nature of the measured magnitudes.

It would be difficult to overestimate the importance of the introduction of the system of fundamental and derived units which is due to the great genius of Gauss. Nevertheless, any particular system of this character is essentially conventional. There is nothing in natural laws which prescribes the choice of any particular measured magnitude, or of any particular number of such magnitudes which may be taken as fundamental. Furthermore, after the establishment of a definite set of fundamental units the derived units are not uniquely determined, nor are their dimensions. It is customary to choose some important relation between the derived magnitudes and the fundamental magnitudes, in order to determine the unit of the derived magnitude and also (through a distinct step which is by no means necessarily consequent upon the first) its dimensions. Thus angle is a typical measured magnitude. It may be expressed in various units. Solid angle may be considered to have the square of the dimensions of plane angle in precisely the same sense that an area can be considered to have the dimensions of the square of a length. Nevertheless, we decide to regard angle as a derived quantity. Having noted the relation that an angle is proportional to the length of an arc divided by the length of a radius, or

$$\text{angle} = \text{const.} \times \text{arc} \div \text{radius},$$

we choose the unit of angle such that the constant is unity. Changing the value of this constant, however, to unity does not affect its dimensions, and it is only by a completely separate step that we make this constant dimensionless by definition, and thus make angle itself dimensionless. Sometimes we find more relations of importance between derived and fundamental quantities than are necessary for the definition of the derived units and dimensions. If we make equal use of all these relations, and are not especially lucky, we shall find that we have conflicting definitions of some of our derived quantities, either with respect to units or to dimensions or to both. But the conflicts may often be removed, either by abandoning one or more of the defining relationships or by changing the set of fundamental units.

The classical example of such a conflict is found in the electric and magnetic units. Gauss proposed that unit electric charge be defined by making the constant equal to unity in Coulomb's law for the force between two charged bodies. It was generally assumed later that this implied fixing the dimensions of charge by making this unit constant dimensionless. Similarly, Gauss proposed to define unit magnetic pole, and this also was assumed to carry with it corresponding implications regarding dimensions. All this would be perfectly satisfactory had it not been for the fact that the principle of Ampère furnished an independent and equally simple method of defining magnetic quantities in terms of purely electric quantities and the fundamental magnitudes, thus leading to another set of units, and presumably also of dimensions, for magnetic quantities.

Thus was created a dilemma which led to a great deal of discussion nearly half a century ago. In the year 1882 in the Philosophical Magazine alone there appeared a dozen papers on dimensions and units by Sundell, Helmholtz, Clausius, and many of the leading physicists of England. Among the latter was Dr. Oliver J. Lodge, who pointed out the striking difference between the points of view of the continental and the English authors. This difference may best be expressed by the statement that the continental authors laid greater stress upon the *units*, while the English authors laid more stress upon the *dimensions* of physical quantities. Thus Helmholtz had no objection to reducing mass to the role of a derived quantity (as indeed had first been suggested by Gauss himself), both with respect to units and dimensions, by employing the law of gravitation as the defining relation, and making the constant of that law numerically equal to unity and also dimensionless, so that he wrote

$$\left[\frac{\mathrm{M}}{\mathrm{L}^2}\right] = \left[\frac{\mathrm{L}}{\mathrm{T}^2}\right].$$

This same line of thought was developed extensively in the very able paper of Sundell. Bridgman states that "Planck was the first to think of the possibility of absolute units." He will find in this paper by Sundell, written in 1882, a very full discussion of many sets of absolute units in which he employs successively various numbers of fundamental units, and determines derived units by making the proper number of fundamental constants each equal to unity. At the same time he makes them dimensionless. For example: "If, in doing this, we wish to make the unit of time a derived unit, we must put

$$1 \text{ sec.} = 31 \times 10^{10} \text{ millimetres.}$$

Time must therefore be expressed as a length." He then shows that by using one set of constants, he obtains "a system in which the unit length is the only fundamental unit. The three electrical units now combine into one."

This last is also true of the dimensional system which I based upon the theory of ultimate rational units (although it is independent of and not necessary for the statement of that theory). In the system that I outlined, not only do the various units and dimensions of electric and magnetic quantities become identical, but the dimensions of all electric and magnetic quantities become integral, thus doing away with the fractional dimensions which are now ascribed to the majority of these quantities, and which many have felt to be a blemish upon the existing system of dimensions.

The paper of Sundell did not receive the attention which was its due, and the whole theory of dimensions, especially of electric and magnetic quantities, fell into confusion which was only apparently alleviated by a well-known paper of Rücker[*], in which he showed that the various systems could be made mutually consistent by assuming that certain dimensions might be regarded as having been "suppressed"—namely, those of di-electric constant and of magnetic permeability. Unfortunately, however, he gave no rule for deciding under what circumstances it was necessary to restore the dimensions which have invariably been suppressed in the definition of every derived quantity. Thus we might decide to restore dimensions that have been suppressed, as we have just seen, in the definition of angle.

Something like this was actually suggested by Williams[†], who proposed to introduce three fundamental dimensions corresponding to length, namely [X], [Y], [Z], so that the dimensions of area would be represented by [XY] and of angle by $[XY^{-1}]$. But even in this method of representing angle, the dimensions, if such there be, inherent in the constant of the relation—angle proportional to arc divided by radius—are still suppressed. Of course, the answer to all such questions is that no quantity whatever has any intrinsic or absolute dimensions, but only the dimensions which we agree to ascribe to it.

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[*] Phil. Mag. xxvii. p. 104 (1889).

[†] Phil. Mag. xxxiv. p. 234 (1892).

One of the reasons for the proposals of Williams was that he objected to having two different types of magnitudes represented by the same unit. The same thought appears to have been in the mind of "O. J. L." when he appended his note to my previous paper, and said that "Length and Mass and Time and Energy and Momentum are not the same. Nor is Temperature identical with Energy. Different things sometimes appear to be of the same dimensions, like Work and Moment of force; but there is an element of direction involved even there, and a scalar product differs from a vector product." Such an element of direction is not always present. If we consider the fraction of a mass of radium which disintegrates per second, we are dealing with a quantity of the same dimensions as the rate of change of a solid angle with the time, and both quantities are scalar. However, no one would think of regarding them as identical. Even using more than three fundamental magnitudes, such coincidences would occasionally occur, and their number will obviously increase as we diminish the chosen number of fundamental magnitudes. Nevertheless, in some cases these coincidences will suggest the existence of hitherto unsuspected identities. For example, those who are familiar with the four-dimensional representation of relativity recognize mass and momentum as two projections of the same vector of extended momentum *, and the fact that the new system of dimensions that I have proposed gives energy the same dimensions as frequency is very suggestive in the light of present views on spectroscopy.

On the other hand, some have objected to the reduction of the number of fundamental magnitudes on the ground that this would restrict the scope and usefulness of the methods of dimensional analysis. This, however, is not the case. All the valid results which are obtainable by these methods can be obtained equally well in a system of any number of fundamental magnitudes. Thus Rayleigh obtained a solution for a certain problem in the interchange of

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* See Wilson & Lewis, Proc. Amer. Acad. xlviii. p. 389 (1912).

heat, using heat and temperature as two additional fundamental magnitudes; but Riabouchinsky [*], employing the mechanical theory of heat and thus adhering to the ordinary simple set of fundamental magnitudes, was unable to obtain the same solution. In his reply Rayleigh said: "It would indeed be a paradox if the further knowledge of the nature of heat afforded us by molecular theory put us in a worse position than before in dealing with a particular problem." So we may also say that the recognition of the velocity of light as a quantity fundamental to all kinematics cannot in any way diminish the content of our previous knowledge.

The whole method of dimensional analysis contains so much that is sound and so much that is unsound that a full logical analysis of the problem has long been needed. Fortunately such a complete analysis in extremely satisfactory form is furnished by a recent paper of Mrs. Ehrenfest [†]. It seems to me that her conclusions are indisputable, and that they clarify to an extraordinary degree the whole problem of the methods of "model" equations and dimensional equations. One of these conclusions is that "The very widespread method of determining, on the basis of the demands of homogeneity, the form of equations as yet unknown, between magnitudes whose dimensions are already fixed, has no foundation and in general may lead to errors."

In other words, if we have a problem of determining the functional relationship between physical variables in a system of which the behaviour is determined by known differential equations, but of such complexity that integration of these equations is inconvenient or impossible, the problem may be solved in identical manner either by the method of dimensional equations or by the method of "model" equations. Both methods lead to identical results, although in using the method of models not a word need be said regarding the dimensions of physical quantities.

On the other hand, for the prediction of an unknown relation between physical quantities, the common method of dimensional analysis has no logical or mathematical basis. If we continue to employ it in the hope that it may lead to useful results, this hope must be based not upon any established principles of science, but upon some vague belief in the simplicity of nature.

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[*] Quoted in Bridgman's 'Dimensional Analysis.'

[†] T. Ehrenfest Afanassjewa, *Math. Ann.* lxxvii. pp. 259–276 (1916).

LXXIX. *Units and Dimensions.*

I WOULD ask Professor Lewis (p. 739) whether he is not attaching undue importance to the numerical part of physical quantities, and trying to regard actual things as if they were or might be pure numbers.

By choosing units we can easily control the numerical part of a specification, and make it 1 if we like; we cannot control the thing itself. The specific gravity of water at 4° is not 1; it is 1 gramme per c.c. The velocity of light is not 1, nor yet 3×10^{10}; it is not a number at all, but a concrete reality.

Arithmetic and counting do not naturally apply to continuous quantities: hence the device of artificial units. Recent Atomism and Discontinuity have given to the operation of counting greater prominence, or at least larger scope, than formerly; for now, surprisingly often, we encounter what seem to be natural units that ask to be counted. But still we must specify what we are counting; otherwise, one might count the oranges, another the bushes, and another the pips.

Every physical quantity has a nature of its own, and it is the reverse of helpful to mask or disregard it. We do not know what an electric charge is, but we know that it is something real and not an abstraction; no mere number can express it. The equation $F = = ee'/K_0r^2$ represents not a convention but a fact of nature. To take K_0 as 1 is a confession that we do not know its real nature and nevertheless wish to employ a practical system of electrical measurement to tide over the time of our ignorance. It would have been equally legitimate, and in some ways more convenient, to take it as 4π; but considerations of that kind are of small importance.

If we prefer to express a charge by counting the electrons on a charged body, then K_0 would be something like $\frac{1}{2}10^{19}$ c.g.s. units. But until we know more, we cannot really measure e or K_0. Nor can we express any Ether quantity dynamically, unless two unknowns cancel out. What we measure is not e but $e/\sqrt{K_0}$.

We may hereafter arrive at a more fundamental dynamics, appropriate to the Ether, and be able to express electric and magnetic quantities in terms of space, time, and some more fundamental conception than mass. Always the actual nature of quantites is the important thing; and about that our statements are by no means conventions, for they may be true or false. If we say that RC is time, that RI^2 is power, that capacity is a length, and that e^2 or $(4\pi e)^2$ is energy × length, we are making fundamental statements; and of these the first two are true, while the last two are false.

I seem to be saying elementary things, and perhaps Professor Lewis agrees with me. If so, I am out of the controversy, which then turns on what units are the most convenient, with our present limited knowledge, for practical purposes. OLIVER J. LODGE.

LXXX. *Semi-optical Lines in the X-ray Spectra.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a paper published in the February number of the Phil. Mag. by Messrs. Bäcklin, M. Siegbahn, and R. Thoræus on "Semi-optical Lines in the X-ray Spectra" (Phil. Mag. vol. xlix. p. 513, Feb. 1925) we have seen that many conclusions on the apparition of X-ray lines in the periodic system and on the electronic structure of the elements are said to be new ones, although they have been pointed out by us more than a year ago (*Journal de Physique et le Radium*, t. v. pp. 1–19, Janvier 1924)*. In the discussion of Mr. Hjalmar's results on the starting up of $K\beta$ and $K\gamma$ lines in the K series of light elements (Phil. Mag. vol. xli. p. 675, April 1921, and *Zeitschrift f. Physik*, vii. p. 341, 1921) we have clearly shown that Mr. Hjalmar's lines cannot be explained in another way, and that, in accordance with our system of atomic structure but in opposition with that of Prof. Bohr, the $K\beta_1$ line just starts up for aluminium and $K\gamma$ for scandium. These statements are well illustrated by the accompanying table and diagram, which are taken from our above-quoted paper; the table was published by us for the first time as soon as 1922 (*Comptes Rendus de l'Académie des Sciences*, t. 175, p. 755, Oct. 1922).

Let us finally note that Messrs. Bäcklin, Siegbahn, and Thoræus ascribe to Stoner (Phil. Mag. p. 286, Oct. 1924) the first idea of the following repartition of the electrons amongst the L levels:

$$2L_3, \quad 2L_2, \quad 4L_1,$$

although this was previously experimentally checked by one

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* In this paper we have denied the relativistic nature of the so-called "regular L doublets," a conclusion which was also later on reached by many authors (Landé, Millikan, and Sommerfeld himself).

N. Bohr et A.Sommerfeld	Regular doublets.	Departure levels.	Irregular doublets.	Equatorial quanta.	Radial quanta.	Latitude quanta.	Azimuthal quanta.
		L_3	}	1	1	0 }	1

of us (A. Dauvillier, *Comptes Rendus*, t. 179, p. 476, Janvier 1924).

We hope that you will have the kindness to publish in your Journal this priority claim and also, if it is possible without trouble, the accompanying table and diagram.

Yours sincerely,
LOUIS DE BROGLIE,
A. DAUVILLIER.

Laboratoire de Recherches Physiques
sur les Rayons X, Paris, 12 rue Lord-Byron,
Feb. 17, 1925.

LXXXI. *On the Electrical Conductivity of Metallic Solid Solutions.* By EUSTACE J. CUY, *Ph.D.*[*]

(Contribution from the Department of Chemistry, Yale University.)

IN a very recent article Höjendahl [†] has discussed "the electrical conductivity and certain other properties of metals and alloys on the basis of the Bohr theory."

In a letter to Professor P. W. Bridgman some time ago (December 16th, 1923) I had expressed some similar views arrived at independently and from different sources of evidence. It may not be out of place to summarize them briefly, since, although in some parts they coincide with those of Höjendahl, in others they complement them.

It is a well known fact that the electrical conductivity of a metal decreases if a second metal is added to it capable of forming solid solutions with it. By solid solution, or mixed crystals [‡], is meant that from the liquid state both substances crystallize together, giving, as far as microscopic examination can detect, a perfectly homogeneous solid phase of variable composition, whose *physical properties vary continuously* from those of pure A to those of pure B. If the specific electrical conductivity is plotted against the composition in per cent. (weight, volume, or mole), a curve very similar to a catenary is obtained. This is not true, if the two pure metals or intermetallic compounds crystallize separately from solution giving a mechanical mixture known as a eutectic. In this case the conductivity-composition ($\lambda - x$) curve is made up of one or more straight lines depending upon the presence or absence of intermetallic compounds [§].

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[*] Communicated by the Author.

[†] Höjendahl, Phil. Mag. xlviii. p. 342 (1924).

[‡] It should be very carefully noted that the very common term "mixed crystals" is a misnomer. It does not signify a mechanical mixture of different kinds of crystals, but a homogeneous crystal of variable composition (mixed with something else).

[§] A very good treatment of this subject is to be found in Tammann's *Lehrbuch der Metallographie*, Voss, Leipzig, 1921, pp. 304-315.

Several attempts to account for the catenary form of the electrical conductivity-composition curve of solid solutions have been made, none of which can at present be considered as successful.

Lord Rayleigh* and Liebenow † have attempted to account for it by assuming that the apparently homogeneous solid solutions consisted of very small submicroscopic particles or plates of the pure components, which at their junctions developed counter-electromotive forces (Peltier effect). This, of course, would tend to decrease the electrical conductivity. Secondary and rather plausible assumptions enabled them to arrive at equations fitting very satisfactorily the experimental results. However, the recently-acquired knowledge as to the structure of crystals by means of X-ray analysis has made their fundamental assumption of submicroscopic inhomogeneity untenable.

Vegard ‡ has found that a KCl–KBr mixed crystal consists of a face-centred K lattice as in pure KCl or KBr and an interpenetrating also face-centred lattice of negative ions of the same lattice constant as the positive ion lattice, also exactly as in KCl or KBr, with the difference, firstly, that the negative ion lattice consists of Cl and Br ions arranged at random, and secondly, that the lattice constant of the mixed crystal is intermediate between that of KCl and KBr. The sharpness of the reflexion maxima, which was as sharp as that of the single salts, shows definitely the absence of groups of Cl or of Br ions arranged in such a way as to constitute even very small KCl or KBr particles microscopically indistinguishable.

Furthermore, Bain § has investigated the solid solutions of Au–Ag and Au–Cu by means of X-rays. In this case also the crystals were perfectly homogeneous. The lattice constant for Au is 4·08 Å., for Ag is 4·05 Å., and for the solid solutions of the two it has an intermediate value. For the alloys of Au–Cu (Cu is 3·60 Å.) the values were again between those of the components. However, there were small deviations from linearity in the direction of greater density (smaller lattice constant).

Another way of accounting for the low conductivity of solid solutions was based on the assumption that the mean free path of electrons in this case was considerably smaller than that in a pure metal, due to the presence at irregular positions of atoms of the second metal. The illustration commonly used was that in a pure metal the atoms were arranged as trees in a garden in definite rows, while a solid solution resembled a forest. A man (electron) could run through the garden much faster than through the forest. It is almost superfluous to state that the recent X-ray work quoted above makes the assumption of irregular arrangement of atoms in solid solutions entirely unjustifiable.

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* Lord Rayleigh, 'The Electrician,' xxxvii. p. 277 (1896); 'Nature,' liv. p. 154 (1896).

† Liebenow, *Zeit. f. Elektrochem.* iv. pp. 201, 217 (1817); Nernst, Theoretical Chemistry,' Macmillan, London, 1911, 6th ed. p. 408.

‡ Vegard, *Zeit. f. Physik*, v. p. 17 (1921).

§ Bain, Chem. & Met. Eng. xxviii. p. 21 (1923).

Rosenhain * has recently proposed an explanation for this phenomenon, best described by the following illustration. If a number of billiard balls of the same size are arranged in a row and the last one is struck, the total impulse will be transferred to the first one. If, however, among them there is one of larger radius, and the last one is again struck, then the large sphere will not transfer all its energy to the adjacent one, but there will be a lateral component which, in so far as direct propagation of energy is concerned, is lost. If such a view is correct, then using an atom of another element having the same radius (in the above illustration, a sphere of another colour but the same size) should not depress the conductivity. A particularly good example is the Au–Ag, system referred to above, whose crystal structure and parameters have been determined by Bain, and whose electrical conductivity has been studied by Matthiessen, Roberts, and Stroudhal and Barus†. The lattice constant of Au is 4·08 Å. of Ag 4·06 Å., and of mixed crystals the same (no shrinkage or expansion on mixing). Consequently the two kinds of atoms are equal in radius. It is therefore hardly to be expected that any decrease in conductivity should occur, since with equal atoms there is hardly any lateral component. And yet the conductivity composition curve is very nearly the same as in the other cases where the radii are unequal. In other words, the atomic radius does not play the role it should if the above explanation were correct.

Schenck ‡ has assumed that the second component does not decrease the mean free path, but decreases the concentration of the electrons. This, of course, would also lower the conductivity. In a sense this cannot be considered as a solution of the problem; it merely changes the question: Why does the presence of B lower the conductivity of A?

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* Rosenhain, Journ. Inst. of Metals, xxx. p. 3 (1923).

† See Tammann's '*Metallographie*,' p. 309 (1921).

‡ R. Schenck, *Phyz. Zeit.* viii. p. 239 (1907).

to: Why does the presence of B lower the electron concentration of A ? *

It is evident that the classical theory of Drude or its various modifications cannot account for this depression of conductivity. J. J. Thomson† has suggested, in order to avoid the difficulty of the equipartition of energy of the electrons, that the electrons arrange themselves in quasi-rigid electron chains having the properties attributed by the classical theory to the individual electrons. It would be expected on this basis that the individual electrons or the electron chain should change their properties (concentration, velocity, mean free path, etc.) continuously upon the addition of a second component, giving a conductivity-composition curve approximately a straight line, but under no circumstances a catenary.

Also the possible explanation, based on the assumption that the amplitude of vibration of the atom passes through a maximum at 50 per cent. composition, making it more difficult for the electrons to travel through the alloy, must be rejected since, in addition to the lack of any theoretical foundation for it, it is empirically found that the conductivity depression is not, as a first approximation, a function of the atomic weight of the second component. This can be seen from the alloys of platinum ‡ with iridium, palladium, gold, rhodium, manganese, copper, and iron §. Similarly, the Cu–Ni and the Cu–Au systems give very similar λ-x curves, although their atomic weights differ by less than 8 per cent. in the former case, and one element is over three times as heavy in the latter.

Bridgman ‖ has suggested that "in metallic conduction the electrons pass through the substance of the atoms, and that the mechanism by which resistance is produced is intimately connected with the amplitude of atomic vibration. The number of free electrons is supposed to remain constant; their velocity is taken to be that of a gas particle of the same mass and temperature, and their mean free path to be many times the distance between atomic centres. . . . . . *There is no necessity in supposing that a single free path is*

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* Compare also Hauer, *Ann. d. Physik*, li. p. 189 (1916), who assumes an equilibrium between the free and the bound electrons.

† J. J. Thomson, Phil. Mag. xliv. p. 657 (1922).

‡ Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, 5th ed., p. 1056 (1923).

§ It should be noted that the conductivity is plotted against the composition in *weight* per cent. The agreement would be very much better if mol. per cent. were used.

‖ Bridgman, Phys. Rev. xvii. p. 161 (1921).

*straight; the electrons may perform Virginia reels about the nuclei of the atoms in quantum orbits**. Something of this sort probably has of necessity to take place in non-cubic crystals."

This, in conjunction with the following suggestion made to the author by Dr. Kurt Fischbeck, formerly of Göttingen, leads to the explanation for the low conductivity of metallic solid solutions. If instead of concentrations their reciprocals are used, then the conductivity of mixed crystals can be calculated on the basis of an equation of the form:

$$\lambda = \frac{\lambda_A}{X_A} + \frac{\lambda_B}{X_B} = \frac{\lambda_A}{X_A} + \frac{\lambda_B}{1-X^A}.$$

where λ, λ_A, and λ_B are the specific conductivities of the solid solution, of A and of B respectively, X_A and X_B the concentrations of A and of B respectively expressed in mol. per cent.† It is evident that the values of λ pass through a minimum at

$$X_A = X_B = 50 \text{ per cent.}$$

It is seen that it is not the concentration that is the important factor, but the groups or clusters of atoms of the same kind through which the electron can pass before coming across one of the opposite kind.

Benedicks ‡ has expressed the opinion that it looks as if atoms had definite channels through which electrons could travel, but which were of such a specific nature (their location, direction, etc., were different in different atomic species), that by mixing atoms of two good conductors the channels were more or less blocked, giving a poor conductor.

The following picture of the cause and mechanism of the conductivity depression due to mixed crystal formation at once suggests itself. At the absolute zero the atoms are at rest, and the electrons are still revolving in their quantum

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* Page 171. The italics are mine.

† This equation would hold for very low temperatures. At more elevated temperatures it would assume the form:

$$\lambda = \frac{\lambda_A}{X_A - K_A} + \frac{\lambda_B}{X_B - K_B} = \frac{\lambda_A}{X_A - K_A} + \frac{\lambda_B}{(1-X_A) - K_B},$$

where K_A and K_B are constants at a given temperature, and prevent the value of the conductivity of the pure metals ($X_A=0$, $X_A=1$) from becoming infinite. These constants are probably in some way related to the gaps present between groups of atoms, as will be discussed below.

‡ Benedicks, *Jahrbuch d. Radioakt. und Elektronik*, xiii. p. 351 (1916).

paths. The valence electrons, to which conduction is due, move in elliptical orbits having a definite frequency of rotation and of perturbation. It does not seem unlikely that these electrons keep in phase. When the electron is furthest from the atom to which it belongs, so are the electrons of all the other atoms. At that instant it is nearest to a neighboring atom. Therefore a potential difference would cause the electron when it is at its greatest distance from its atom, instead of returning to its own atom, to jump across to the not very distant quantum path of the neighbouring atom, thus accounting for the supra-conducting state.

This in a sense bridges over the Haber * theory of an independent electron lattice moving through the metal, the Thomson † theory of rigid electron chains moving in certain directions, and the Bridgman ‡ theory that resistance is caused by the difficulty of an electron jumping from atom to atom.

In a solid solution at the absolute zero the atoms are again at rest and the electrons revolving, but they are not now in phase, since the frequencies of rotation and of perturbation for the electrons of each atomic species are different. This accounts for the fact that supra-conductivity is not observed in solid solutions. In other words, the "gap trouble" does not exist since all the atoms are at rest, but the "phase trouble" does since two different kinds of atoms are mixed together.

Professor Bridgman has called my attention to the fact that recently some alloys of Sn and Pb and also some amalgams have been found to assume supra-conductivity. The Pb–Sn system does not give complete solid solutions (the metals are not miscible in all proportions in the solid state), but Pb contains 4 per cent. of Sn, and Sn only 1 per cent. of Pb. From the phase-rule diagram it appears that the solubility of the two metals in each other decreases on cooling. It is therefore possible that either or both metals may throw off all the foreign constituent at very low temperatures. In any case, however, the foreign atoms are very few. The amalgams, on the other hand, usually give eutectics (mechanical mixtures) of the pure metals as in the case of Hg–Zn, or of intermetallic compounds as in the case of Hg–Li or Hg–Na. As Professor Johnston has remarked, it is not necessary that all the metallic mass become supra-

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* Haber, *Sitzb. preuss. Akad.* pp. 506, 990 (1919).

† J. J. Thomson, Phil. Mag. xliv. p. 657 (1922).

‡ Bridgman, Phys. Rev. xvii. p. 161 (1921).

conducting, since a few coherent threads of one supra-conducting metal are sufficient to cause the classification of the alloy as supra-conducting. It is, however, extremely probable that systems like Au–Cu, Ag–Au, etc., which give complete solid solutions, will never be found to exhibit supra-conductivity.

As the temperature is raised, the atoms will begin to vibrate and bigger and bigger moving gaps will appear, making it more difficult for electrons to jump from atom to atom—that is, causing an increase in resistance according to Bridgman's view.

In a metallic solid solution this gap source of resistance will be present to the same extent as in the pure metals at the same temperature. In addition, there will be the difficulty due to the electrons of unlike atoms not being in phase. Therefore a configuration which would have allowed an electron to jump to the next atom in a pure metal will not do so in an alloy—that is, the resistance will be greater. This is known to be the case.

Raising the temperature a given number of degrees will cause a given increase in resistance for reasons explained above. In a solid solution, however, this increase in the number and magnitude of the gaps will not have as great an effect as it did in the case of a pure metal, where it was the only source of resistance. To illustrate: in a pure metal, out of 100 possible electron jumps, 30 say are hindered by the accident that the atoms are far apart at that instant; in a solid solution, out of 100 possible jumps, 50 say do not occur, due to the fact that the electrons of adjacent foreign atoms are not in phase, and 30 per cent. of the other 50 due to the gaps. Therefore the temperature coefficient of the resistance of solid solutions will be less than that of pure metals (15 per cent. as against 30 per cent. in the example given). This is in agreement with the experimental observations.

Bridgman has found that, in general, pressure renders metals better conducting. This, of course, is to be attributed to the fact that the gaps are made smaller by pressure. By analogous reasoning to that given above about the effect of temperature, it can be shown that the pressure-coefficients of solid solutions should be less than that of their components. This is also in agreement with experimental observations, since cases are known where the coefficients of alloys are not only smaller but even negative.

The well-known fact that the physical and chemical properties of components of an alloy (such as atomic weight, valence, molecular volume, lattice constant, etc.) do not, as a first approximation, show themselves in the conductivity-composition curve is, of course, to be ascribed to the fact that the electron orbits are not a simple function of any of these variables. The great similarity of all λ-x curves is to be attributed to the fact that they all represent probabilities of favourable conditions making an interatomic jump possible.

The fact that, although the addition of a second metal to form a solid solution lowers the electrical conductivity very greatly, the addition of a third or fourth has relatively small effect * can be attributed to the small number of groups of atoms of A or of B which the addition of C or D can break up, since the presence of B has already made impossible the existence of any large number of atoms of A grouped together. Therefore our view that the increase in resistance due to the formation of solid solutions can be attributed to the absence of large groups of atoms of either kind, accounts for the smaller and smaller effect that additional components have upon the conductivity of an alloy.

It is not at present clear how the Franz-Wiedemann ratio could be derived for alloys from the views here given.

The phenomena described above will have to be explained by any generally valid theory of metallic conduction. They have up to the present been, to a large extent, neglected by physicists.

Summary.

A brief review of the theories of electrical conductivity has been given with particular emphasis on their application to metallic solid solutions. It is found that none of the accepted theories will account for the observed phenomena.

If it is assumed that the electrons responsible for metallic conduction move in quantum orbits, and in a pure metal are in phase with those of the adjacent atoms, then the following facts can be accounted for:—(1) The low conductivity of alloys consisting of one kind of crystals of variable composition; (2) their low temperature coefficient; (3) their low pressure coefficient; (4) the absence of the supra-conductive state; (5) the great similarity of the conductivity-composition curves of various mixtures, and (6) the absence of any specific effects due to the physical and chemical properties of the second metal added.

August 28, 1924.

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* Fischbeck, *Zeit. f. anorg. Chem.* cxxv. p. 1 (1923).

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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[SIXTH SERIES.]

MAY 1925.

LXXXII. *Radiation given out by Gases through which Electric Discharges are passing.* *By* Sir J. J. THOMSON, *O.M.*[*]

IN a paper on the electric discharge through gases at low pressures (Phil. Mag. July 1924) I gave reasons for thinking that the ionization in the "negative glow" is due to radiation excited by the cathode rays in the gas through which they pass.

The following paper contains an account of a series of experiments made with the object of obtaining direct evidence of the existence of this radiation and of throwing some light on its properties and origin. This radiation is not penetrating enough to pass through the glass of the discharge-tube, so that to study it we must use some method by which it can be detected inside the tube or, at any rate, before it has had to pass through an appreciable thickness of solid matter.

The most sensitive methods for detecting such radiations depend on the electrical effects, such as those of ionization or of photo-electricity, which they produce. As the electrical discharge fills the tube with ions which would disturb any electrical detector of the radiation if they came into contact with it, it is necessary to screen off the ions from the detector.

I have used three kinds of screens: the first of these is a material screen of very thin celluloid; in the second there is no solid matter between the detector and the gas in the tube, but the ions are screened off by a strong electrostatic field; in the third type of screen the electrostatic field is replaced by a magnetic one.

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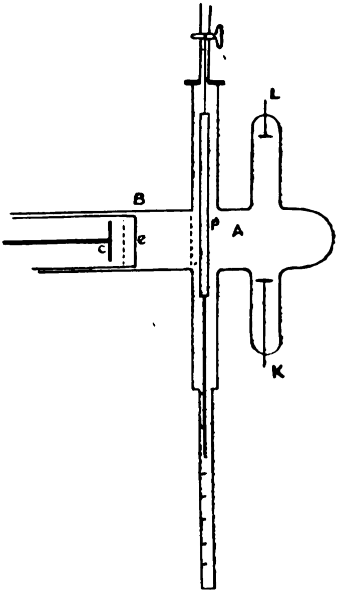
[*] Communicated by the Author.

I shall commence with the experiments made with the first type of screen. My assistant, Mr. Everett, has found a very convenient way of making screens of this kind: a drop of a very weak solution of celluloid in ether is put on the top of a pool of mercury and allowed to evaporate, leaving a thin circular disk of celluloid floating on the mercury, from which it can easily be detached. From very weak solutions it is easy to get celluloid disks thin enough to show brilliant colours of thin plates and whose mass per unit area is less than that of a layer 1/10 of a millimetre thick of air at atmospheric pressure. These films are very tough although they are so thin, and one about a centimetre in diameter can sustain without rupture a difference of pressure on its two sides of several millimetres of mercury.

Fig. 1.



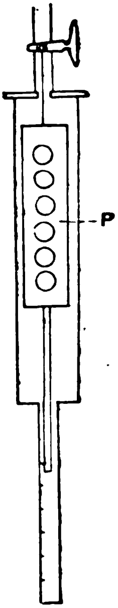
The arrangement used to detect the radiation with a screen of this kind is shown in fig. 1. K is the cathode and L the anode of a discharge-tube. When the discharge passes, the cathode rays pass through the gas in front of K and produce the dark space and the negative glow.

A horizontal side tube B is fused on to the tube A at a place in front of the cathode so that the radiation from the negative glow passes down this tube; the portion of the tube A opposite B is blown out so as to prevent the impact of cathode rays on the glass opposite B. The detector of the radiation is placed in a tube which fits into B. This detector consists of a metal disk *c* carried by a metal rod, which is carefully insulated and connected with one pair of quadrants of a Dolezalek electrometer. The sensitiveness of the electrometer was such that it gave a deflexion of 300 scale divisions per volt. As very wide ranges of current had to be measured a battery of condensers, giving a capacity which could be varied from ·001 to 1 microfarad, was arranged so that any capacity within these limits could be added to the electrometer. The capacity of the electrometer system and its connexions with the disk was ·00014 mf. The rod and disk are surrounded by a metal tube connected with the earth. The end of this tube nearest to the discharge-tube is closed by one of the thin celluloid films *e* just described; wire gauze connected with the earth is placed in front of and behind the film so as to shield the disk *c* from electrostatic induction arising from charges of electricity in the discharge-tube. The other end of the tube carrying the celluloid disk *e* is closed and a wire from *c* to the Dolezalek passes through an ebonite plug in this end of the tube. The disk *c* in most of my experiments was about 2 mm. from the celluloid film and was very nearly of the same diameter (1 cm.) as the film itself.

This arrangement in which a screen of celluloid is used has many advantages; thus, as there is no communication between the tube enclosing the disk and the tube through which the electrical discharge passes, the pressure of the gas round the disk *c* can be altered without affecting the pressure of the gas in the discharge-tube; this is an important point, for valuable evidence as to the effects produced by the radiation can be obtained by altering the pressure of the gas round *c*. The disadvantage of this method is that before the radiation can be investigated it has to pass through a film of celluloid. We shall see later on that of the radiation coming from the negative glow only a fraction of one per cent. gets through a film of celluloid so thin that it shows brilliant colours of thin plates and thus could not have been much more than 3×10^{-5} cm. thick. This arrangement is thus not suitable for studying the most absorbable type of radiation, though it is the most convenient for studying radiation "hard" enough to penetrate the film in appreciable amounts. I shall, before proceeding to discuss the more absorbable radiations, describe some of the results which have been obtained with this type of detector.

To measure the absorption of the radiation by different substances so as get some idea of its wave-length, the following arrangement was used. A plate of lead pierced with six circular holes, the size of the celluloid window, could be moved vertically up and down by a cord passing over a winch, as shown in fig. 2. This plate passed quite close to the celluloid window, between it and the negative glow. Of the six holes in the plate one was left open, another was closed by a celluloid film of the same thickness as that used for the screen, another was covered by aluminium-foil 5×10^{-6} cm. thick, another by two layers of this foil, the fifth by gold-leaf 7×10^{-6} cm. thick, and the last by two layers of this leaf; thus, by comparing the effect produced on the disk *c* when the winch was turned so as to bring the free opening in the plate in front of the window with that when it was turned so as to bring either the aluminium, gold-leaf, or celluloid into this position, the absorption by these substances could be determined.

Fig. 2.



The electric discharge through the tube was produced by a high potential dynamo made by Evershed and Vignolles, which gave steady potential differences up to 5500 volts; for higher voltages an induction coil was used; experiments were also made using a hot tungsten filament for cathode.

When the electric discharge is passing through the tube and the cathode rays are traversing the gas in front of the window, the electrometer connected with the disk *c* is deflected, showing that the disk is receiving a charge of electricity. Before the discharge starts the quadrants of the electrometer connected with *c* are put to earth, the other pair of quadrants are permanently earthed, then if *c* is disconnected from earth and the discharge started, there is a deflexion of the electrometer, continuously increasing at first, but ultimately attaining a constant value; the amount and even the sign of the deflexion depends upon circumstances, such as the pressure of the gas in the discharge-tube, the potential difference between the electrodes of the tube, to some extent upon the position of the anode, and also upon the pressure of the gas round the disk connected with the electrometer.

The electrical effects which the radiation might be expected to produce are (1) photoelectric effects, (2) effects due to the ionization of the gas between the disk *c* and the earthed wire gauze.

Let us consider the effect on the electrometer produced by the photo-electric effects. In consequence of this effect, the radiation falling on *c* would cause it to to emit negative electricity: this would leave *c* and the electrometer with a positive charge; whereas, except when the pressure in the tube containing *c* is very low and the potential difference large, the charge in the electrometer is generally negative. If this negative charge is due to photo-electric effects it must be because the photo-electric effect of the celluloid film is greater than that of the disk, so that the stream of negative electricity coming from the film towards the disk is greater than that going from the disk towards the film. If this were the explanation of the negative electrification of the disk, then if instead of the celluloid screen we used one consisting of a strong electric field, the disk ought always to acquire a positive charge, as there is no other photo-electric source of negative electrons to counterbalance the stream coming from the disk itself; we shall see, however, that with these electrostatic screens the charge in the electrometer is frequently negative. This proves that in some cases the most important factor is not the photo-electric effect, but must arise from the ionization of the gas between the disk *c* and the gauze. This negative charge would result from the negative electrons diffusing more rapidly to the disk than the positive ions; the disk would charge up negatively and accelerate the flow of the positive ions and retard that of the negative until the flow of the one was equal to that of the other.

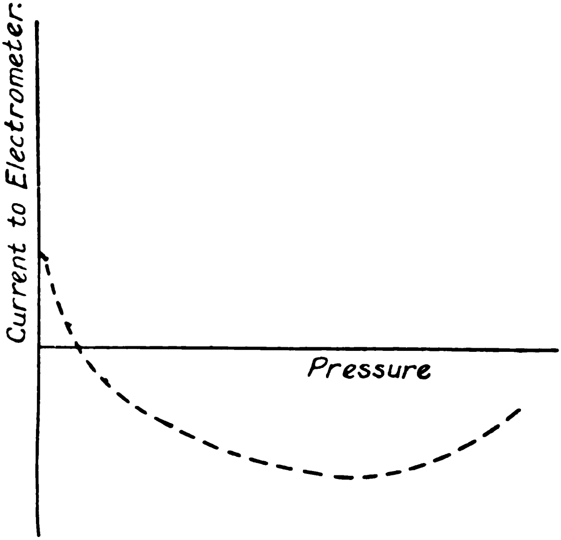
In addition to the effect due to the difference of the rates of diffusion, the experiments give some evidence that, when the gas is ionized by the radiation, more electrons are emitted in the direction in which the radiation is travelling than in the opposite direction, so that a stream of ionizing radiation is accompanied by a stream of electrons in the same direction.

Very direct evidence as to the importance of the ionization effect on the charges received by *c* is obtained when we investigate the effect of altering the pressure of the gas round *c*, while leaving that in the discharge-tube unaltered;

the form of apparatus shown in fig. 1 enables us to do this without difficulty, as there is no communication between the tube through which the electric discharge passes and the one round *c*.

Starting with a very low pressure round *c* and gradually increasing it, we find that the rate at which *c* receives negative electricity increases with the pressure of the gas, and at some stages the rate of increase of the deflexion of the electrometer is more rapid than the rate of increase in the pressure. The rate of increase with the pressure finally falls off as the pressure round *c* gets greater, and there is often a pressure at which the rate of charging up has a maximum value.

Fig. 3.



The range of pressures round *c* used in these experiments was from that of the best vacuum which could be obtained by the use of charcoal cooled by liquid air to about 4 mm. of mercury, which was about the greatest pressure the celluloid film would stand without breaking. When the pressure round *c* was exceedingly low, *c* generally received a positive and not a negative charge. The relation between the rate of charging up of the disk *c* (the ordinate) and the pressure of the gas round *c* (the abscissa) is of the character represented in fig. 3, when the discharge is produced by the continuous high-tension dynamo and the potential difference is from 1000 to 5000 volts.

These results show, I think, that in this case the negative charge is due to the ionization effects; these would vanish in a perfect vacuum, and would increase with the pressure of the gas round *c*.

The photo-electric effects tend to give the electrometer a positive charge, while the effects due to ionization tend to give it a negative one; thus the charge acquired by the electrometer may be positive or negative according as one or other of these effects predominates. Increase of pressure round *c* will increase the ionization effects relatively to the photo-electric ones and thus tend to make the charge given to the electrometer negative. Increase in the "hardness" of the rays in the discharge-tube will favour the photo-electric effect, because the harder rays are not so readily absorbed by the gas between *c* and the gauze and so do not produce so much ionization as the softer ones. This effect can readily be observed by using an induction coil to produce the discharge and gradually diminishing the pressure in the discharge-tube by means of a tube filled with charcoal coolod with liquid air. When the pressure is fairly high (say ·1 mm. of Hg) and the discharge goes easily, as shown by the shortness of the equivalent spark-gap, the electrometer will receive a negative charge, but as the pressure falls and the spark-gap increases the negative charge will diminish, will vanish, and then be replaced by a positive one.

In the preceding experiments the cathode is placed so that the cathode rays do not strike against those parts of the walls of the discharge-tube which have a view of the window through which the radiation passes on its way to the testing apparatus; if the cathode rays are bent by a magnet so as to strike against the parts of the glass walls of the discharge-tube opposite to the window the charges received by the electrometer are very much increased.

Character of the Radiation in the Tube.

The character of that part of the radiation in the tube which is able to penetrate the celluloid window of the testing apparatus can be determined by measuring the ratio of the rate of charging up of the electrometer when screens of various substances are put before the celluloid window to the rate when no such screens were interposed. The results of such measurements are given in the following table. The thickness of the celluloid film was estimated from its optical properties as about 3 10^{-5} cm. The thickness of the gold screen was such that 100 sq. cm. of the leaf weighed ·014 gr., that of the aluminium such that 100 sq. cm. weighed ·0142 gr. The discharge was produced by the high potential dynamo. In the table, *r* represents the ratio of the rate of charging up of the electrometer when the underwritten screen was inserted to the rate before insertion.

Gas in the discharge-tube—hydrogen.

Potential difference between the electrodes 1500 volts.

r. Celluloid.	*r.* Aluminium.	*r.* Gold.
·4	·3	·125

Potential difference between the electrodes 5000 volts.

·6	·6	·16

Gas—helium.

Potential difference between electrodes 1500 volts.

·5	·38	·12

Potential difference 5000 volts.

·6	·57	·18

Gas—oxygen.

Potential difference 1500 volts.

·47	·38	·125

Potential difference 5000 volts.

·52	·45	·15

If μ is the coefficient of absorption of the rays by aluminium, ρ its density, and t its thickness, since 100 cm.^2 weighed ·0142 gr.,

$$10^2 \times \rho \times t = \cdot 0142\,; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

while at 1500 volts, taking the mean of the absorptions for aluminium,

$$\epsilon^{-\mu t} = \cdot 36,$$

so

$$\mu t = \cdot 95,$$

so that from (1)

$$\frac{\mu}{\rho} = 6 \cdot 7 \times 10^3.$$

For the K radiation of chromium, whose wave-length is $2 \cdot 2 \times 10^{-8}$, μ/ρ is equal to 136. If we assume the usual law connecting the absorption of the radiation with its wave-length λ, *i. e.* that μ varies as λ^3, the wave-length corresponding to $\mu/\rho = 6 \cdot 7 \times 10^3$ is $8 \cdot 1 \times 10^{-8}$ cm.; the voltage corresponding to this radiation is 1500 volts, which is exactly the voltage applied to the discharge-tube. It must be remembered that all the radiation, even when there is no screen before the celluloid window, has to pass through this window before reaching the detector, and that any radiation soft enough to be absorbed by the window would not be detected by this method; we shall see directly that by far the greater part of the radiation in the tube is so absorbed, so that by this method we are dealing only with the most penetrating radiation.

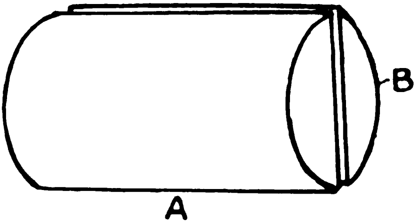
It will be seen by the comparison of the results given in the table on p. 768 for potential differences of 1500 and 5000 respectively that the rays which pass through the celluloid film get on the average more penetrating as the potential difference applied to the discharge-tube increases. The character of this radiation thus depends on the potential difference. I made a large number of experiments to see if it depended on the nature of the gas in the discharge-tube. I measured the coefficients of absorption in aluminium, gold, and celluloid with air, oxygen, hydrogen, and helium in the discharge-tube, and with the same potential difference between the electrodes could not be sure that there was any difference in the radiation produced by the change of gas; the difference, if any, is certainly small: these observations only refer to the harder radiations which can pass through the celluloid film. The amount of radiation is less in the light gases than in the heavy ones.

The type of radiation in a tube with a given gas at constant pressure may depend upon the means used to send the discharge through the tube; thus the type of radiation depends to some extent upon whether the discharge is produced by a continuous-current dynamo or by an induction coil, and if by an induction coil, upon the size of the coil and the nature of the interrupter. This might be expected, as the potential difference between the electrodes often depends upon the character of the discharge and is not determined solely by the pressures.

Very "Soft" Radiation in the Tube.

In the previous method all the radiation has to pass through a celluloid film before reaching the detector, so that only the "rays" hard enough to pass through the film come under observation. To study the more absorbable types of radiation I have used screens by which the ions in the discharge-tube are screened off from the detecting apparatus connected with the electrometer, not by material screens, but by screens of intense electric and magnetic forces. One arrangement I used is shown in fig. 4.

Fig. 4.



The halves A and B of a cylindrical brass rod fit tightly into a glass tube fitted into the tube which holds the disk attached to the electrometer. A and B are insulated carefully from each other and are connected respectively with the poles of a battery of small storage-cells so that potential differences up to 1000 volts can be maintained between them. The distance between the plain faces of A and B is 1 mm., and their length 3 cm. A simple calculation will show that when the difference of potential between A and B is 600 volts (the difference most frequently used in these experiments), any ions, whether positive or negative, attempting to pass between A and B would be driven against one side or the other unless their energy were greater than that corresponding to well above 100,000 volts. This was also established directly by experiment, as long before the difference of potential between A and B reached 600 volts an increase in the potential difference produced no effect on the deflexion of the electrometer. The fact that over very wide ranges of potential difference the deflexion is independent of the potential shows that no appreciable radiation is produced by driving the ions against the sides of the slit.

When this arrangement was put in place of the celluloid screen ions would be stopped, but the radiations would reach the detector without passing through any matter other than the gas in the tube; this is a great advantage. The disadvantages are, firstly, since A and B have to be close together to get a strong electric field, the area of the window through which the radiation from the discharge passes is much less than when the celluloid film is used; and secondly, since there is direct communication between the discharge-tube and the one surrounding the detecting apparatus the pressures in these two tubes are always the same, whereas when the film is used either of these pressures can be varied independently of the other.

I have also used a strong magnetic field instead of an electric one to screen off the ions, but found the electric one the more convenient.

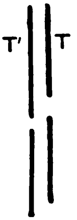
Absorption of Rays by the Celluloid Film used in the previous experiments.

We can measure by the electrostatic screen how much of the radiation was stopped by the celluloid. As one of the openings in the sliding plate (fig. 2) can be stopped by a film of the same thickness as that used for the window in the first experiments, all we have to do is to measure the rate of charging up of the electrometer, (1) when a free opening in the moving plate is opposite the slit of the electric screen, and (2) when an opening filled by the celluloid film is in the same position. The results are very remarkable: with oxygen in the discharge-tube and a potential difference of 3000 volts between the electrodes, the rate of charging of the electrometer when the radiation did not pass through the celluloid was more than 100 times greater than when the rays passed through it. So that in the previous experiments we have only been dealing with a small percentage of the radiation in the tube; the great bulk of this radiation when the potential is comparable with 3000 volts is completely stopped by a layer of celluloid about $3 \cdot 10^{-5}$ cm. thick. By moving the lead plate carrying the various diaphragms up and down we can insert screens of celluloid, aluminium, and gold in the path of the radiation and find the absorption produced by them. The relative amounts of the soft radiation stopped by these screens differ from those for the harder radiation which in the earlier experiments had been filtered through a celluloid screen. Thus with the harder radiation the gold always transmitted far less than either the aluminium or the celluloid (see p. 768), while with the softer radiation passing through the electrostatic screen the gold transmits twice as much as the aluminium or celluloid. I noticed, many years ago, in some experiments I made on very soft Röntgen rays generated by low-speed electrons from a hot cathode, that relatively to aluminium gold absorbed much fewer of the softer than of the harder rays. This, I think, is due to much of the radiation having wave-lengths comparable with the characteristic radiations of aluminium and carbon, so that the absorption of these substances is abnormal.

The conflict between the photo-electric effect and the ionization one is shown quite as distinctly with the electric screen as with the celluloid one. For when the pressure is fairly high we find that with the electric filter the electrometer receives a negative charge, but as the pressure is diminished the negative charge changes to a positive one. At the higher pressures the ionization has the upper hand, and this produces a flow of electrons to the electrometer, the photo-electric effect produces a flow of electrons from the disk, and this tends to make the charge in the electrometer positive; this effect does not diminish as the pressure diminishes, while that due to the ionization does, so that at very low pressures the electrometer must acquire a positive charge.

To make sure that the charge acquired by the electrometer arose from the effect of radiation and was not due to the passage of gas in some abnormal state between the jaws of the electric screen, I tried the following experiment. I placed in front of the jaws of the electric screen the screen represented in fig. 5 made of two sheets, T and T′, of thick tinfoil with holes bored through them as in the figure. This screen was opaque to radiation travelling in the direction necessary to get through the electric screen, but was pervious to a flow of gas from one side to the other. This screen stopped completely any charging up, positively or negatively, of the electrometer. Hence we conclude that this charging is due to radiation coming from the discharge-tube.

Fig. 5.



The preceding experiments show that a tube through which an electric discharge is passing is filled with radiation, some of which is of an exceedingly absorbable type, so absorbable that it is practically stopped by the equivalent in mass of a layer of air at atmospheric pressure a few millimetres thick.

The proportion which these very absorbable radiations bear to the other radiations in the discharge-tube depends upon a great variety of circumstances, on whether for example the discharge is produced by an induction coil or by a steadily-maintained potential difference. The amount of radiation in the discharge-tube has covered a very wide range in these experiments. Taking as the unit the deflexion per second of the electrometer when connected up with a condenser whose capacity is ·1 microfarad, the output of radiation has varied from ·001 to 4·5. The results of these experiments show that when the output is large there is a much larger proportion of the more absorbable rays than when it is small.

The fraction of the radiation passing through one layer of gold leaf when oxygen was in the tube has varied from 1/36 to 1/1000 The larger value occurred with a steady difference of potential equal to 4000 volts, the pressure was ·015 mm. of Hg and the output of radiation ·015. The smallest value was when the discharge was produced by an induction coil: the output of radiation was 3·4, the equivalent spark-gap 5 mm., and the pressure ·003 mm.

In hydrogen the range of absorption produced by the gold-leaf was from 1/80 to 1/400, the largest value was obtained with a hot lime cathode under a constant potential difference of 3000 volts at the pressure ·045 mm., and an output of ·08, the smallest value with an induction coil, spark-gap 4 mm., output 2·2, and pressure ·042 mm.

In helium the fraction getting through the gold-leaf varied from 1/40 to 1/300, the largest occurred with the discharge from a coil with an output ·36, pressure ·084 mm., the smallest when the coil had an output of 3, pressure ·062. Films of silver and aluminium showed similar effects, though their absorption was greater than that of the gold-leaf.

Absorption of radiation by gas.

The negative glow may be well developed when the pressure in the discharge-tube is as low as ·01 mm. of mercury. If, as we have supposed, the ionization in the negative glow is produced by the soft radiation, then this radiation must suffer appreciable absorption when passing through a layer of gas at this pressure comparable in thickness with the linear dimensions of the negative glow, say 10 cm. The mass of a layer of gas 10 cm. thick at the pressure ·01 mm. of mercury is equivalent to that of a layer of air 1/760 mm. thick at atmospheric pressure, this has about the same mass as a celluloid film 10^{-7} cm. thick. Films as thin as this are not manageable, so we cannot by means of them detect whether there is any radiation in the discharge-tube as soft as that indicated.

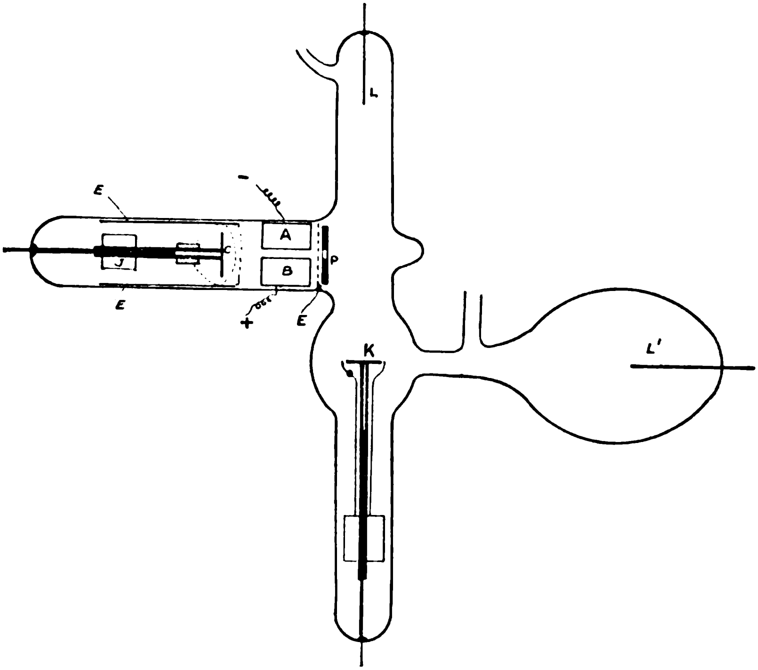
Absorption of radiation by air.

We can, however, by the following method test the absorption produced by the passage of the radiation through different lengths of the gas actually in the discharge-tube.

The arrangement is that represented in fig. 6.

The disk *c* and the wire gauze in front of it are rigidly connected with a metal tube which can slide along the metal rod connecting the disk *c* with the electrometer. A piece of iron J is attached to the tube and this can be made to move backwards and forwards along the tube by a magnet. The wire gauze in front of the disk is insulated from it and is kept connected with earth by a thin wire spring. By altering the distance of the disk from the end of the electric screen we can alter the length of path traversed by the rays before they reach the disk, and by making measurements when the disk is in different positions we can determine the absorption of the rays when they pass through a known length of gas at the pressure in the discharge-tube. For these experiments the opening in the electric screen was stopped down until the aperture was so small that all the rays passing through it fell upon the disk even when it was moved to the most distant position at which measurements were made.

Fig. 6.



Experiments with this apparatus gave very interesting results, these varied with the nature of the gas and the pressure in the tube, but observations made with oxygen at the pressure ·01 mm. bring out many of the points of interest.

When the disk is close up to the electric screen the electrometer receives a *negative* charge, indicating the predominance of the ionization effect; as the disk is moved further away from the screen the rate at which the electrometer receives a negative charge diminishes, until when the distance between the disk and the screen is about 15 mm. the electrometer does not charge up either positively or negatively. After passing this point the electrometer acquires a *positive* charge, indicating that now the photo-electric effect is predominant; the positive effect increases up to a maximum when the distance of the disk from the end of the electric screen is about 30 mm., after this it begins to diminish and goes on diminishing continuously as the distance between the disk and the screen is increased to its limiting value, 50 mm. Thus, as the length of path of the radiation through the gas increases the character of the radiation changes, just as the colour of non-homogeneous light changes when it passes through a medium which absorbs one colour more than another.

With the radiation we are considering, which includes a continuous spectrum, the radiation of longer wave-length, which is the more efficacious in providing ionization, is the more easily absorbed, and thus absorption would make the negative effects due to ionization diminish more rapidly as the length of path of the radiation through the gas increases than the positive effects due to photo-electricity, so that at a certain distance the latter may begin to predominate. As radiation of all kinds is absorbed to some extent, there will be a distance at which the positive effect is a maximum. This explanation is confirmed by the results which are obtained when the pressure is altered; thus when the pressure is considerably lower than that in the last experiment the positive effect is the only one observed, even when the disk is put quite close up to the electric screen; it reaches a maximum at a distance from the screen depending upon the pressure and then diminishes. At these low pressures the ionization effect is relatively less important than the photo-electric one and so is not able to overpower it. On the other hand, at pressures considerably higher than ·01 mm. the negative effect is the only one observed, and this diminishes continuously as the distance between the disk and the screen is increased. These experiments show I think conclusively that even at the low pressures occurring in the discharge-tube there is an appreciable amount of absorption of the radiation and therefore the production of an appreciable amount of ionization in the space of a few centimetres of gas.

Similar experiments were made with hydrogen and helium, and it was found that the pressures at which the change from the negative to the positive effect occured was far higher in hydrogen than in oxygen, and again far higher in helium than in hydrogen. This is what we should expect as the negative effects are due to the absorption of the rays, and this absorption at equal pressures is much greater in oxygen than in either hydrogen or helium.

Amount of absorption by the gas in the discharge-tube.

The radiation in this tube is very complex, it is probable that it is in the main a continuous X-ray spectrum up to a frequency ν where $h\nu = Ve$; here V is the potential difference between the electrodes in the tube and h Planck's constant. Superposed on this there will be those characteristic radiations of the gases in the tube which have a frequency less than ν. The absorption of the different parts of the spectrum will vary rapidly with the wave-length of the radiation, and as we do not know the distribution of energy among the various wave-lengths, we cannot do more than form an estimate of an average value of the absorption.

In the case we have just been considering an increase of 1·5 cm. in the distance through which the radiation travels changes the sign of the effect, and after a further increase of 1·5 cm. the positive effect is a maximum, while another 2 cm. reduces the positive effect to about two-thirds of its maximum. This shows, I think, that the intensity of a considerable part of the radiation must be reduced to $1/\epsilon$ of its value in a length comparable with about 3 cm. This corresponds to a coefficient of absorption in oxygen equal to 1/3 at ·01 mm. pressure. This is equivalent to an absorption coefficient of $2{\cdot}53 \times 10^4$ at atmospheric pressure. The absorption coefficient at this pressure in air for the K radiation of iron, whose wave-length is 1·93 Å, is 2×10^{-2}, hence, assuming that the absorption is proportional to the cube of the wave-length, the wave-length of the very absorbable radiation we are considering would be about 200 Å, the energy corresponding to this radiation is about 60 volts.

The intense absorption of the radiation by gases has an important application to the theory of the structure of light. It shows I think that the region in which the energy of this very absorbable radiation is concentrated, the quantum, must be considerably greater than the region occupied by an atom. For the radiation to be absorbed the quantum must pass over an electron, and when the absorption occurs in a few millimetres of the gas at the pressure of ·01 mm. of mercury, the quantum must have a cross-section considerably greater in area than that of a circle whose radius is 10^{-8} cm., if it is to meet with one electron while passing over the distance within which it is absorbed. Thus the quantum would have to be of atomic dimensions, even if every collision with an electron resulted in absorption, an exceedingly improbable assumption. From what we know of the absorption of radiation, particularly its variation with the wave-length, it is much more probable that the quantum has to make on the average a considerable number of collisions with electrons before absorption takes place, this would require the cross-sections of the quantum of these very absorbable radiations to be considerably greater than the cross-section of atoms. I gave in the 'Philosophical Magazine,' Sept. 1924, a theory of the structure of light in which the quantum is regarded as a ring made up of lines of electric force, the circumference of which is equal to the wave-length of the light. For the characteristic radiation from the heavier elements the wave-length is considerably smaller than atomic dimensions, but for the soft radiations we are considering the wave-length is several times greater than the atomic radius.

Radiations from different parts of the discharge.

The luminosity of the discharge in the neighbourhood of the cathode varies enormously at different distances from the cathode, thus we have at the surface of the cathode a thin layer of velvety glow, this is succeeded by the dark space which emits very little visible light, following this we have the bright luminosity of the negative glow ; the transition from the dark space to the negative glow is often, as in oxygen, exceedingly abrupt, and the position of the boundary can be determined to the fraction of a millimetre. It is important from the point of view of the theory of the discharge to ascertain if this large variation in luminosity is accompanied by a corresponding variation in the emission of the ionizing radiation. To test this I arranged that the cathode K, fig. 6, could by means of a magnet be moved backwards and forwards along the tube ; when the cathode was as far back as possible, the negative glow was opposite the slit through which the radiation passed to the testing apparatus; as it was moved forward various parts of the negative glow came at first in front of the slit, then the negative glow passed beyond the slit and was succeeded by the dark space, various parts of the dark space then passed in front of the slit until finally the cathode itself went past the slit.

The following example shows the kind of variation that is found in the radiation coming from different regions near the cathode, the length of the dark space in this experiment was 30 mm. :—

	Distance of slit in front of cathode.	Radiation.	Fraction passing through gold-leaf.
Dark space	0	10	1/150
	10 mm.	25	1/120
	20 mm.	23	1/125
	30 mm.	18	1/108
Glow	40 mm.	15	1/216

Thus, there is a falling off in the intensity of the radiation close to the cathode, but otherwise there is a steady increase in the radiation as we proceed from the negative glow into the dark space, the gas in the discharge-tube was oxygen at the pressure of ·014 mm. There was bright luminosity in the negative glow and a sharply-defined boundary between the negative glow and the dark space, so that there was discontinuity in the brightness of the luminosity. It will be seen from the figures that there was no indication of any abrupt variation in the emission of the absorbable ionizing radiation. In addition to the amount of the radiation coming from the different parts of the discharge I measured also the absorption of this radiation by gold-leaf at different places, the results are given in the third column, it will be seen that the rays from the part of the negative glow furthest from the cathode are the most easily absorbed, and that inside the dark space there is not much variation until we get quite close to the cathode when the rays become of a softer type.

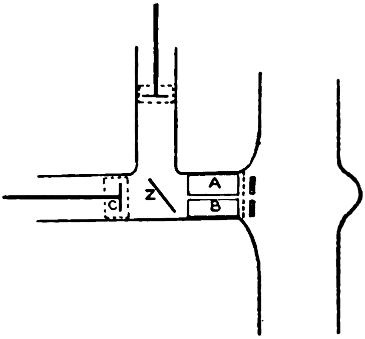
Similar results were found when the gas in the discharge-tube was hydrogen or helium, though in those gases the changes in the luminosity are not so abrupt as in oxygen.

When the direction of the discharge was reversed, so that the electrode K, fig. 6, was anode, and L or L′ cathode, ionizing radiation could be detected coming from the region near the anode ; it was, however, small compared with that coming from near the cathode, although when an induction coil was used the current passing through the tube was much larger when L′ was cathode than when it was anode.

Reflexion of the Rays.

Experiments were made to see if any reflexion could be obtained from polished metallic surfaces. For this purpose the following arrangement was used. Z is a brightly polished disk of zinc, supported by a rod placed in a horizontal tube which joins the main tube B just behind the two pieces of brass A, B which form the electrical filter ; a vertical tube provided with an insulated disk connected with the electrometer and provided with arrangements for measuring the electrical effect, is fused to the tube so as to be above Z and in such a position that rays reflected from Z would strike the disk in this tube. The rod supporting the disk Z could by the action of a magnet on a piece of iron attached to it be pushed forward, so as to be in the path of the radiation coming from the discharge, or drawn back in the tube so as to allow the radiation to strike against the disk *c*. The rod could also be turned round by a magnet and the disk rotated through a considerable angle. Measurements were made first with Z drawn back in the tube and the disk *c* connected with the electrometer, we shall call the deflexion of the electrometer the direct effect. The disk Z was now pushed forward and the electrometer connected with the disk in the vertical tube. Z was now rotated and it was found that when it was in a certain position there was an appreciable deflexion of the electrometer ; that this is due to a true reflexion of the rays is shown by the fact that the deflexion of the electrometer ceases when Z is rotated through a small angle in either direction from the position in which the deflexion is a maximum. The reflector Z was connected to a positive potential of 600 to prevent the emission of electrons.

Fig. 7.



The ratio of the reflected to the direct effect varied with the potential difference between the electrodes of the discharge-tube ; it was greater when the potential difference was large than when it was small, the maximum I observed when oxygen was in the discharge-tube was 7 per cent. With hydrogen in the tube the value of this ratio was smaller, never in my experiments exceeding 5 per cent. ; while in helium it was much smaller, the maximum value being one-half of one per cent.

The other side of the zinc disk was covered with a smooth layer of paraffin wax. There was a slight deflexion of the electrometer when the disk was rotated through 180° so as to replace the polished zinc reflector by a paraffin one, the effect was, however, small—generally about 1/7—of that produced by the polished surface.

These experiments show that when cathode rays pass through a gas Röntgen rays are generated. These rays are not all of one kind, some of them have wave-lengths very much shorter than those corresponding to the characteristic radiation of the gas, the indications are that they form a continuous spectrum, the limiting frequency ν being given by Planck's relation, $h\nu = \mathrm{E}$ where E is the energy of the cathode ray. Very little seems to have been done on the generation of the continuous Röntgen ray spectrum by the passage of electrons through gases. We may as a guide to what may be expected try to connect the absorption of Röntgen rays by a gas on which a great many experiments have been made with the emission of the rays by the impact of electrons. Let us suppose that we have an enclosure at a temperature high enough to include Röntgen rays among the radiation ; the energy of rays having a frequency between ν and $\nu + d\nu$ is by Planck's law, when $\epsilon^{-h\nu/\mathrm{R}\theta}$ is small, proportional to

$$\epsilon^{-\frac{h\nu}{\mathrm{R}\theta}}\nu^3 d\nu,$$

and the number of quanta per unit volume having energy between these limits is therefore proportional to

$$\frac{1}{h}\epsilon^{-\frac{h\nu}{\mathrm{R}\theta}}\nu^2 d\nu.$$

Now suppose that there are molecules of a gas in this enclosure, these will absorb the radiation and to keep things in a steady state must give out on the average as much radiation as they absorb. The number of quanta striking a molecule of the gas in unit time will be proportional to

$$\epsilon^{-\frac{h\nu}{R\theta}} . \nu^2 c . d\nu,$$

where c is the velocity of light. Assuming that the absorption is proportional to the cube of the wave-length, *i.e.* to $1/\nu^3$, the chance of one quantum being absorbed on collision varies as $1/\nu^3$; hence the number of quanta of Röntgen radiation absorbed by the molecule per second is proportional to

$$\epsilon^{-\frac{h\nu}{R\theta}} . c . \frac{d\nu}{\nu} .$$

Now let us consider the emission, which we shall suppose is due to the impact of electrons. The number of electrons having velocities between v and $v+dv$ is proportional to

$$\epsilon^{-\frac{mv^2}{2R\theta}} . v^2 dv.$$

The number of these which collide with the molecule in unit time is proportional to

$$\epsilon^{-\frac{mv^2}{2R\theta}} v^3 dv.$$

Let us suppose that the chance of their producing a Röntgen ray of frequency between ν and $\nu+d\nu$ is

$$f\left(\frac{mv^2}{2}, \nu\right) d\nu.$$

Then the emission of the rays will be proportional to

$$d\nu \int_{v_1}^{\infty} \epsilon^{-\frac{mv^2}{2R\theta}} v^3 f\left(\frac{mv^2}{2} . \nu\right) dv.$$

Where the lower limit of v is given by the equation

$$\tfrac{1}{2} m v_1^2 = h\nu,$$

this integral since the emission is equal to the absorption must be equal to

$$\epsilon^{-\frac{h\nu}{R\theta}} c \frac{d\nu}{\nu} .$$

A solution of this integral equation is

$$f\left(\frac{mv^2}{2}, \nu\right) = \frac{C}{\frac{mv^2}{2} \nu} .$$

So that the chance of an electron producing a quantum of radiation whose frequency is between ν and $\nu+d\nu$ is proportional to $\frac{1}{T}\frac{d\nu}{\nu}$, where T is the kinetic energy of the electron. Since the energy in the quantum is $h\nu$, the energy emitted will be proportional to

$$\frac{d\nu}{T}.$$

The value of ν will depend on the circumstances of the collision, such as the smallest distance between the electron and the centre of the atom, or of some of the electrons in the atom. The maximum value of ν will be equal to T/h; we shall give reasons for thinking that there may be a minimum whose frequency is equal to that which just produces ionization in the gas. When we have a great many electrons all having approximately the same energy, the energy in the radiation having frequencies between n_1 and n_2 emitted per second by a given number of molecules is proportional to

$$\frac{n_1-n_2}{T}.$$

The total quantity of energy radiated is obtained by putting $n_1=T/h$, and $n_2=T_0/h$ where T_0 is the energy required to ionize the gas; using these values in the preceding expression we find that the average energy generated by a single collision of electrons, all having the same amount, T, of kinetic energy is proportional to

$$1-\frac{T_0}{T}$$

and thus as soon as T gets large compared with T_0, is nearly independent of the kinetic energy. The electrons with large amounts of energy give radiations over a larger range of frequencies than those with smaller amounts, but the density of the energy is not so great. Though at each collision the fast electron may not produce much more radiant energy than the slow one, yet it can make many collisions before its energy gets so much reduced that it is unable to generate Röntgen radiation, so that the total amount of radiant energy produced by the fast one will be much greater than that produced by the slow.

On the average, the energy contributed to the continuous spectrum for one collision will be independent of the energy of the electron. The number of collisions an electron makes before losing its energy is proportional to the square of the energy (J. J. Thomson, 'Discharge of Electricity through Gases,' 2nd Edition, p. 378), hence the energy in the Röntgen radiation produced by a given number of electrons will be proportional to the square of the energy of the electrons, a result which has been confirmed by a large number of investigators.

Hitherto we have not considered what determines the wave-length of the radiation produced when an electron with a given amount of energy strikes against an atom. In the case of the emission of the characteristic radiation from an atom, the radiation seems to occur when an electron loses potential energy by falling from a place where this is great to one where it is smaller, the potential energy lost instead of being converted into an increase in the kinetic energy of the electron is converted into radiant energy, and the frequency of the radiation, ν, is given by

$$h\nu = \text{loss of potential energy.}$$

Now when an electron passes through an atom and comes into collision with its electrons it is at some part of its path losing potential energy. In a collision with an electron the maximum loss of potential energy will be e^2/c, where c is the minimum distance between the electron in the atom and the moving electron. If the frequency of the radiation emitted is related to this loss of energy by Planck's law, then

$$h\nu = \frac{e^2}{c},$$

i.e. ν is inversely proportional to c, so that λ the wave-length of the radiation is proportional to c. If the energy T of the electron is large compared with e^2/c, c and therefore the wave-length will differ very little from b, the perpendicular from the fixed electron on the initial direction of motion of the moving one. Let us see if this will lead to the result that the probability of the emission of radiation of frequency between ν and $\nu + d\nu$ is proportional to

$$\frac{1}{\mathrm{T}} \cdot \frac{d\nu}{\nu}.$$

The probability of an electron making a collision such that b is between b and $b + db$ is proportional to $2\pi b \,.\, db$.

If $\mathrm{F}(\mathrm{T} \,.\, b)$ is the probability that this collision results in the emission of a quantum of radiation $\mathrm{F}(\mathrm{T} \,.\, b) 2\pi b \, db$ must be proportional to

$$\frac{1}{\mathrm{T}} \frac{d\nu}{\nu}.$$

Since ν varies as $1/b$, $F(T\,.\,b)$ must be proportional to

$$\frac{\cdot 1}{Tb^2}.$$

Now the energy transferred at the collision between two electrons is

$$T\bigg/\left(1+\frac{b^2T^2}{e^4}\right),$$

or when T is large compared with $e^2\,b$, to e^4/Tb^2. Thus the chance of a quantum being emitted is proportional to the energy lost by the electron in the collision.

It follows from this way of looking at the question that there will be a maximum value of λ, for when b is large compared with the distance between the electrons in the atoms, the electric field through which the electron passes will not be the field due to a single electron, but one due to the action of several electrons and the positive charge. The electric field of the electron passing outside the atom will be the "stray" field of the atom, and the variations in the potential energy in this field may be very much less than e^2/b, where b is the distance from the atom. Thus when b exceeds a value comparable with the radius of the atom very little energy will be transformed into radiation.

There will in the discharge-tube be a continuous degradation of the primary Röntgen radiation into secondary, tertiary, and so on, radiation of longer wave-length. For the primary radiation produced by the cathode rays will be a continuous spectrum with a fixed limit; this radiation when absorbed by the gas will cause it to emit electrons covering a wide range of speeds, but none having a speed exceeding that of the original cathode rays. These secondary electrons will give rise to trains of secondary Röntgen radiation, these trains will be continuous spectra, but the limiting frequency will in each case be less than that for the primary radiation. Supposing there was no loss of energy in this process, the energy in the secondary radiation would be concentrated into a shorter range of frequencies than the primary radiation. If the secondary radiation were by a similar process converted into tertiary radiation, the range of frequencies in the tertiary radiation would be less than that in the secondary, and so on. Thus these transformations would all result in the continuous Röntgen-ray spectrum getting shorter and shorter and more and more energy being concentrated in the region of the longer wave-lengths.

We have left out of account the effect of collisions with other electrons on the energy of the electrons ejected by the radiation; if the energy of these electrons was greater than the mean energy of electrons at the temperature of the enclosure, the ejected electrons would on the whole lose some of their energy before giving rise to the secondary radiation. This would tend still further to increase the wave-length of the secondary radiation in comparison with that of the primary and so increase the rate at which radiation of a shorter wave-length than that of the mean wave-length corresponding to the temperature of the enclosure was degraded into radiation of a longer wave-length. On the other hand, if the wave-length of the primary radiation were longer than the mean, the electrons it ejected would have less energy than the average of that of the electrons in the enclosure; collisions with these electrons would increase their energy and this would diminish the wave-length of the secondary radiation. By this process the wave-length of the secondary radiation might be diminished below that of the primary. We see from this that there are agencies at work to increase the wave-length of the short radiations and diminish those of the long ones, and those bring about a distribution of wave-lengths in statistical equilibrium.

A stream of homogeneous radiation of frequency ν ejects electrons with energies equal to $h\nu$, and these electrons will give rise to a continuous spectrum of Röntgen rays where the upper limit of the frequency is equal to that of the primary beam. This secondary system will give rise to other systems whose average wave-length is greater than its own. Thus the homogeneous primary beam will be accompanied by a continuous spectrum of radiation, the wave-length of the radiation increasing with the distance from the primary beam. The time taken for the transformation of the corpuscular radiation excited by the primary Röntgen rays into the continuous Röntgen spectrum will be inversely proportional to the velocity of the ejected electrons, which will, except for very hard primary rays, be small compared with the velocity of light. Thus the primary beam will travel through a considerable distance before the transformation is completed, so that the tail will be a very long one. This continuous spectrum would constitute scattered radiation, distinct from the normal type of scattered radiation which is not accompanied by a preliminary transformation of the primary Röntgen radiation into corpuscular radiation. The latter will be of the same frequency as the primary radiation, whereas the new radiation will form a continuous spectrum with the frequency of the incident radiation as the upper limit of its frequency. Again, the variation of the intensity of the scattered radiation with the angle between the incident and scattered rays will not be the same in the two cases.

Summary.

An account is given of experiments on the radiations inside a closed vessel containing gas at a low pressure through which an electric discharge is passing. It is shown that, when electrons pass through gases, Röntgen rays are produced which may be of far higher frequency than any of the characteristic radiation of the gas. Thus, when electrons produced by a potential difference of 1500 volts passed through hydrogen, Röntgen radiations having a frequency corresponding to 1500 volts were found. The spectrum appears to be a continuous one with its maximum frequency proportional to the energy of the electrons. Some of this radiation is absorbed by gases with remarkable rapidity; thus, for example, radiations were detected in the tube which were absorbed in 2 or 3 cm. of air at the pressure ·01 mm. of Hg. Absorption as great as this shows that the volume in which the energy of this type of radiation is concentrated must be considerably larger than the volume of a molecule of the gas. It is shown that there is some regular reflexion of the radiations from a polished metal surface, the maximum amount of reflexion obtained being about five per cent.

An expression is arrived at for the distribution of energy in the continuous spectrum produced when electrons pass through a gas.

I have much pleasure in thanking my assistant, Mr. Everett, for the help he has given me in making these experiments.

LXXXIII. *The Theory of the Drift of Projectiles.*

By E. T. Hanson, *B.A.*[*]

Introduction.

THE investigation of the motion of a spinning shell through the air is not only of great practical importance, but also of considerable theoretical interest. The complete treatment is very difficult, and there are still many parts of it that require further investigation. The whole problem is very fully and ably treated in "The Aerodynamics of a Spinning Shell," Phil. Trans. ser. A, vol. ccxxi., by Messrs. Fowler, Gallop, Lock, and Richmond.

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[*] Communicated by the Author, who is indebted to the Admiralty for permission to publish this paper.

In the present short communication an extension of the Particular Integral of the approximate equations of motion is discussed. The shell is considered to be a rigid spinning body acted upon by three forces at right angles to one another passing through the centre of gravity, and by three couples about axes at right angles to one another which intersect at the centre of gravity. The problem cannot be solved generally; approximate solutions only can be obtained by certain simplifying assumptions.

Now there is one assumption about the legitimacy of which there can be little doubt. A projectile is symmetrical about its axis of spin. When it is travelling "nose on," that is when the axis is tangential to the path of the centre of gravity or, in other words, when the "Yaw" is zero, the motion of the projectile is that of a particle under the combined forces of gravity and "drag." Excepting the couple tending to reduce the spin, which couple is usually very small, all the remaining components of the force system vanish with the yaw.

Instead of putting any restrictions upon the force system called into play by the reaction of the air, the following conditions are assumed to be satisfied :—

(*a*) The spin is large or, as will be explained, sufficiently large to justify the approximations involved.

(*b*) The yaw, which is the angle made by the axis of the shell with the tangent to the path of the centre of gravity, is always small.

(*c*) The deviation of the path of the centre of gravity from the plane normal trajectory is always small.

While keeping the force system as general as possible, the initial velocity of the shell is considered to be largely arbitrary. The theory is interesting as indicating the nature of the changes produced in the drift as the spin of the shell is gradually increased without limit.

The plane trajectory is defined as the path described by the shell in space when it is treated as a particle.

Theoretically, the foregoing conditions are merely assumptions, but practically it is not too much to say that, unless they are justified, the trajectory would be in most cases useless in actual gunnery. With regard to the spin, its magnitude is dependent upon the rifling of the gun, and therefore largely controllable.

In the case of the yaw, the condition (*b*) is certainly complied with in practice, when the shell is initially stable, at all points of every trajectory which does not exceed an initial elevation of about 45°. The formula for the drift of a shell has been shown to depend very approximately upon the ratio of two of the components of the force system. But this result depends upon experimental evidence as to the magnitude of the forces, which indicates that the ratio is small. It is not a consequence of the conditions laid down above. Assuming these conditions only, it is shown under what circumstances this ratio must be small. Those cases are then considered in which it is possible to treat the components of the force system very generally. An apology must be made for treating the notation somewhat carefully in the next section. Much difficulty is often caused by lack of appreciation of this important detail.

The Force System and Coordinate System.

Let O be the centre of gravity of the shell, and OXYZ a system of rectangular coordinates. Let OY be the direction of motion of the centre of gravity at any instant, and let XOY be the plane which contains the axis of spin initially, so that the angular precession is measured from XOY. Let OB be the direction of the axis of spin at any instant. Then the angle BOY is the yaw of the shell. The angle which the plane BOY makes with XOY is the angle of precession.

Let $BOY = \phi$

and let the angle of precession $= \psi$.

Let OA be perpendicular to OB and in the plane BOY, which is the plane of yaw. Let OC be perpendicular to OA and OB. Let OA′ and OC′ be the positions which OX and OZ would respectively take up if they were rotated about OY through an angle ψ.

The force system due to air resistance is then defined as follows:—

The drag R acting along YO.

A force $R_1 \sin\phi$ acting along OA′.

A force $R_2 \sin\phi$ acting along OC′.

A couple M acting about OB and tending to reduce the spin.

A couple $M_1 \sin\phi$ acting about OA, tending to turn OB into the position OC.

A couple $M_2 \sin\phi$ acting about OC, tending to turn OB into the position OA.

$R_1R_2M_1M_2$ being quite arbitrary, the factor $\sin\phi$ is justified by the assumption that these forces vanish with ϕ. Through O construct a plane perpendicular to the plane trajectory and cutting the latter in G. Let OY′ be parallel to the tangent at G in the direction of travel, and let OX′ be parallel to the normal at G drawn outwards. Let OZ′ be drawn to the right of the plane trajectory. Let the plane XOY cut the plane Y′OZ′ in OW. In order to make the foregoing systems of reference quite precise, it is only necessary to adopt the following convention :—

As the centre of gravity moves, the plane XOY always contains OX′.

Let the angle $Y'OW = \alpha$ and $YOW = \gamma$.

Let OX′ make with the vertical an angle θ. Since α and γ are assumed to be small, α is the deviation of the direction of motion of the centre of gravity from the tangent to the plane trajectory to the right, and γ is the deviation upwards. Let the velocity of G along the plane trajectory be noted by v. To the approximation required this is the velocity of O. Let Ω be the spin of the shell, m its mass and C its moment of inertia about its axis of spin.

The Equations of Motion.

When a shell leaves the muzzle of a gun, the motion of its axis is frequently of a highly oscillatory character. The initial values of $\dot{\phi}$ and $\dot{\psi}$ may be such as to set up rapid vibrations of period comparable with that of the spin. These vibrations take place about a mean steady motion of the axis, which is comparatively slow. This mean steady motion gives rise to the trajectory, which is known as the "mean twisted trajectory."

The approximate theory of these vibrations has been dealt with in various places, and there is evidence to show that they gradually subside. It is not intended here to consider the theory of these oscillations under a completely general force system, but it is assumed that the initial values of $\dot{\phi}$ and $\dot{\psi}$ are such that the shell describes its mean twisted trajectory, without oscillations of its axis, from the moment when it is clear of the muzzle blast. These are, in fact, the conditions usually selected for the "particular integral" of the approximate equations of motion. Under these circumstances $\dot{\phi}$, $\dot{\psi}$, and, of course, $\dot{\theta}$ may all be considered small compared with Ω.

The general equations of motion have been fully dealt with elsewhere. In the present notation, except for the force system, they are given in a paper entitled "The Initial Motion of a Projectile" (Phil. Mag. xlvi. p. 1027). Under the conditions here laid down the last two of equations (8) of that paper reduce to

$$\left.\begin{aligned} -C\Omega\Omega_2 &= M_1 \\ \text{and} \qquad C\Omega\Omega_1 &= M_2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

With regard to the validity of these equations, they theoretically imply little restriction upon the force system, assuming that we may make the spin as great as we please. The value of ϕ may be initially large, but the greater it is initially the more rapidly is it damped out (see equation 8 below). The force components upon which $\dot{\psi}$ depends must be kept within limits, and in fact they are in practice small enough to justify the application of (1) in the derivation of the approximate formula for drift.

These two equations (1) combine into the single complex equation

$$\left.\begin{aligned} \frac{\partial}{\partial t}(\phi e^{i\psi}) + \dot{\theta} + \gamma + i\dot{\alpha} &= -\kappa\phi e^{i\psi}, \\ \text{where} \qquad \kappa &= \frac{M_1 - iM_2}{C\Omega} \end{aligned}\right\} \quad . \quad . \quad . \qquad (2)$$

The equations (4) and (5) of the same paper, when reduced, combine into

$$\left.\begin{aligned} \dot{\gamma} + i\dot{\alpha} - \frac{g}{v}\sin\theta(\gamma + i\alpha) &= f\phi e^{i\psi}, \\ \text{where} \qquad f &= \frac{R_1 - iR_2}{mv} \end{aligned}\right\} \quad . \quad . \quad . \quad . \qquad (3)$$

The slightly altered notation and generalization of the force system require no further explanation.

The Solution of the Equations.

It is convenient to write

$$\phi e^{i\psi} = p \quad \text{and} \quad \gamma + i\alpha = q.$$

The equations (2) and (3) then become

$$\dot{p} + \kappa p + \dot{\theta} + \dot{q} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

$$\dot{q} + \tan\theta \, . \, \dot{\theta}q - fp = 0, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

making use of the well-known equation of the plane trajectory

$$\dot{\theta} = -\frac{g}{v}\cos\theta.$$

Under the conditions laid down, the formulæ (4) and (5) are quite general.

Since $$\tan\theta\,.\,\dot{\theta}=-\frac{g}{v}\sin\theta,$$

equation (4) may be written

$$\dot{p}+(\kappa+f)p-\frac{g}{v}\cos\theta+\frac{g}{v}\sin\theta\,.\,q=0. \quad . \quad . \quad . \quad (6)$$

Now let us consider trajectories whose initial elevations do not exceed 45°. These are sufficient for our purpose, and it will be shown that they can be treated with considerable accuracy and simplicity. There is no justification for omitting $\dot{q}$ in (4), for over a large part of most trajectories $\dot{q}$ may be quite comparable with $\dot{\theta}$ without contravening condition (c). This latter condition requires that q should be small, and therefore, initially, the last term of (6) will be small compared with the penultimate term. But since $\sin\theta$ decreases and $\cos\theta$ increases until the vertex is reached, we have an additional justification for assuming that the last term is entirely negligible in its effect upon the yaw.

The equation (6) may therefore be written

$$\dot{p}+(\kappa+f)p+\dot{\theta}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The complementary function is obtained by omitting $\dot{\theta}$. It is

$$p=\phi e^{\iota\psi}=\phi_0 e^{-\int(\kappa+f)dt}, \quad . \quad . \quad . \quad (8)$$

if the initial values of ϕ and ψ be ϕ_0 and zero respectively. The complementary function is, therefore, damped out, and is also oscillatory in character. When substituted in (5) it results in the "mean twisted trajectory" and produces no permanent drift.

The particular integral can be written

$$p+\frac{\dot{\theta}}{\kappa+f}+\frac{\ddot{\theta}}{(\kappa+f)^2}-\frac{\dot{\theta}(\dot{\kappa}+\dot{f})}{(\kappa+f)^3}+\ldots\ldots=0.$$

Now $\ddot{\theta}$ is always very small, and the rate of change of the force system is taken to be never large. Hence, if one of the components of κ or f be moderately large, the third and remaining terms of this expression are quite negligible.

Hence for the particular integral we have

$$p=-\frac{\dot{\theta}}{\kappa+f}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Substituting (9) in (5), we obtain

$$\frac{\partial}{\partial t}\{q\sec\theta\}=-\frac{f}{\kappa+f}\sec\theta\,.\,\dot{\theta}, \quad . \quad . \quad . \quad (10)$$

for it is unjustifiable to assume here that $\dot{\theta}q$ is negligible.

If f be large compared with κ, the factor $f/(\kappa+f)$ may be treated as sensibly constant. In any case, if this factor be constant the equation can be completely solved.

The solution required can be expressed in the form

$$\dot{q}=\frac{f}{\kappa+f}\dot{\theta}\left[\sin\theta\log\tan\left(\frac{\pi}{4}+\frac{\theta}{2}\right)-1\right]. \quad . \quad . \quad (11)$$

Hence at the vertex

$$\dot{q}=-f\dot{\theta}/(\kappa+f),$$

and therefore, unless f be small compared with κ, the condition (c) will not be satisfied.

If, on the other hand, f is small, we may write (10) in the form

$$\frac{\partial}{\partial t}(q\sec\theta)+\frac{f}{\kappa}\sec\theta\,.\,\dot{\theta}=0. \quad . \quad . \quad . \quad . \quad (12)$$

In practice the only components which need be retained are M_2 and R_1, so that

$$\frac{f}{\kappa}=i\frac{R_1}{M_2}\cdot\frac{C\Omega}{mv}.$$

In this case (12) is equivalent to Mayevski's equation for drift in its generalized form.

Considering now those cases in which $\dot{\theta}$ is small, of the same order as $\dot{q}$, (5) may be written

$$\dot{q}-fp=0,$$

so that, from (9),

$$\dot{q}=-\frac{f}{\kappa+f}\dot{\theta}.$$

This equation may easily be discussed generally, but for convenience and brevity consider, as before, only the components M_2 and R_1, and let the ratio R_1/M_2 be constant.

Let $f=\rho$ and $\kappa=-i\mu$, and note that ρ/μ is proportional to the spin.

Then

$$\dot{\gamma}=-\frac{\rho^2}{\mu^2+\rho^2}\dot{\theta}$$

and

$$\dot{\alpha}=-\frac{\mu\rho}{\mu^2+\rho^2}\dot{\theta}.$$

If the ratio ρ/μ be treated as a variable parameter, then, for a given point on the trajectory, γ will increase continuously from 0 to $\theta_0-\theta$ as ρ/μ increases from 0 to infinity. Under the same circumstances α will increase from 0 to a maximum $\frac{1}{2}(\theta_0-\theta)$, and will then decrease to zero. This maximum occurs when the ratio ρ/μ is unity.

Thus under no circumstances can the vertical drift do more than counteract the effect of gravity, nor can the lateral deviation exceed half the maximum value of the vertical deviation. Only when the ratio ρ/μ is less than unity can the lateral deviation exceed the vertical.

LXXXIV. *The Flow of Water in an Inclined Channel of Rectangular Section.* *By* HAROLD JEFFREYS, *M.A., D.Sc., Fellow and Lecturer of St. John's College, Cambridge* *.

1.0. IT is well known that water flowing in pipes obeys the laws of viscous flow so long as the velocity does not exceed a certain limit depending on the viscosity and on the dimensions of the pipe, but that if the velocity exceeds this limit the motion ordinarily becomes turbulent and the frictional stress becomes proportional to the square instead of the first power of the velocity. The corresponding problems relating to the flow of a fluid over a plane seem to have received much less attention from the experimental side, though it is generally believed that the laws followed are very similar. The frequent occurrence in nature of turbulent flow over a plane or nearly plane surface, with a free surface for the upper boundary, suggested that a direct experimental determination of the coefficient of skin friction and of the Reynolds criterion for turbulence in such a case was desirable. Such an investigation is described in the following pages. A determination of the Reynolds criterion in similar conditions has been previously made by L. Hopf †, but he did not find the coefficient of skin friction when the critical speed was much exceeded, and the methods adopted differ materially in the two cases.

2. THEORY.

2.1. *Purely viscous flow.*—Let α be the inclination of the surface to the horizontal, and let axes of x and z be taken, x along the direction of greatest slope and z perpendicular to the plane. Let u be the velocity, ζ the depth, and ν the kinematic viscosity. Then if the channel be of uniform width, we have the dynamical conditions

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* Communicated by the Author.

† *Ann. d. Phys.* (4) xxxii. pp. 777-808 (1910).

$$\frac{du}{dt} = g \sin \alpha - \frac{1}{\rho}\frac{\partial P}{\partial x} + \nu \frac{\partial^2 u}{\partial z^2}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$0 = -g \cos \alpha - \frac{1}{\rho}\frac{\partial P}{\partial z}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where P denotes the pressure and g the intensity of gravity. The vertical acceleration has been neglected, since it is essentially an insignificant fraction of g. We have, further, the equation of continuity

$$\frac{\partial \zeta}{\partial t} = -\int_0^\zeta \frac{\partial}{\partial x}(u\zeta)\,dz. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In steady flow (3) is an identity, and (2) shows that so long as $\partial\zeta/\partial x$ is not comparable with $\tan \alpha$, the pressure term can be omitted from (1). This being the typical case, the solution of (1) must be

$$u = \frac{g \sin \alpha}{2\nu}(2z\zeta - z^2), \quad . \quad . \quad . \quad . \quad . \quad (4)$$

since this satisfies the boundary conditions, namely that u is zero in contact with the bottom, where z vanishes, and that $\partial u/\partial z$ is zero at the surface. The surface velocity is

$$u_1 = g \sin \alpha \,.\, \zeta^2/2\nu, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the mean velocity, taken with regard to the depth below the surface, is

$$u_0 = g \sin \alpha \,.\, \zeta^2/3\nu, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

so that the mean velocity is necessarily 2/3 of the surface velocity.

The rate of flow of fluid across a unit length perpendicular to the direction of flow is

$$Q = u_0\zeta = g \sin \alpha \,.\, \zeta^3/3\nu. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If then Q and ν are specified, the depth and the velocity at any depth are determinate. Conversely, if we can measure Q and u_1 or ζ, we can find ν.

2.2. *Turbulent flow.*—With the same notation, save that u will be taken to denote the mean velocity at the depth under consideration (*i.e.*, eddy velocities are supposed averaged out), let the frictional force per unit area over the bottom be $\kappa\rho u_1^2$, where ρ is the density and κ the numerical constant of skin friction. The condition for the water to be unaccelerated is that

$$\kappa u_1^2 = g\zeta \sin \alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

The ratio of the mean velocity to the surface velocity is subject to some uncertainty. If it be m, we have

$$Q = mu_1\zeta = m(g \sin \alpha \,.\, \zeta^3/\kappa)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

$$= m\kappa u_1^3/g \sin \alpha. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

If m be known, a determination of Q and of u_1 or ζ will enable us to find κ.

In turbulent flow there is always a region of laminar flow with rapid shearing close to the solid boundary. If the velocity at the boundary between the turbulent and non-turbulent regions is nu_1, and if the thickness of the non-turbulent region is l, which is by hypothesis small compared with ζ, the conditions at the solid surface are:

$$u = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

$$\nu \frac{du}{dz} = \kappa u_1^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

If then l be so small that we can neglect $l^2 d^2u/dz^2$, we have

$$\nu n u_1/l = \kappa u_1^2,$$

that is

$$l = \nu n/\kappa u_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

Again, let us suppose that the conditions in the turbulent layer can be represented by a uniform coefficient of eddy viscosity k. Then within this layer we must have

$$u = u_1 - \frac{g \sin \alpha}{2k}(\zeta - z)^2, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

so that

$$(1-n)u_1 = g \sin \alpha \,.\, \zeta^2/2k, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

with our approximations. The mean velocity in the turbulent layer is $(\frac{2}{3} + \frac{1}{3}n)u_1$, and that in the non-turbulent layer is $\frac{1}{2}nu_1$. Thus the mean velocity over the whole depth is given by

$$mu_1\zeta = (\zeta - l)(\tfrac{2}{3} + \tfrac{1}{3}n)u_1 + l \,.\, \tfrac{1}{2}nu_1, \quad . \quad . \qquad (9)$$

so that practically

$$m = \tfrac{2}{3} + \tfrac{1}{3}n. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

A determination of the velocities at the surface and at the boundary of the non-turbulent layer will therefore give the mean velocity. Further, we have from (8) and (1)

$$2k = \frac{g \sin \alpha \,.\, \zeta^2}{(1-n)u_1} = \frac{\kappa^2 u_1^3}{(1-n)g \sin \alpha}$$

$$= \frac{\kappa Q}{m(1-n)} \quad . \quad . \quad . \quad (11)$$

by (3).

Thus the eddy viscosity is determinate. Again, we readily see from (6) that the smallness of l/ζ requires that Q/ν shall be large compared with nm/κ. If this condition is not satisfied, the non-turbulent layer will take up a considerable part of the depth of the liquid, and an important correction will be needed to allow for it.

2.3. *The Reynolds number.*—It can as usual be shown from dynamical similarity that the resistance to the motion of a fluid over a plane must be of the form

$$F = \kappa \rho u_1^2 . f(Q/\nu) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The no-dimensional parameter Q/ν will here be used as the Reynolds criterion. It has the advantage that both Q and ν are directly under control, the former by regulating the supply of water, the latter by varying the temperature or the amount of dissolved material.

When Q/ν is very great, f is practically unity; when it is small, we easily find from 2.1 that

$$f\left(\frac{Q}{\nu}\right) = \frac{4}{3}\frac{\nu}{\kappa Q} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The form of this suggests that the transition from purely viscous to turbulent motion will take place when Q/ν is in the neighbourhood of $4/3\kappa$. The transition need not, however, be sudden.

3. EXPERIMENT.

3.1. I am much indebted to the courtesy of Prof. Inglis for being allowed to carry out the following experiments in the Hydraulics Department of the Cambridge Engineering Laboratory, and to Mr. R. R. M. Mallock for the loan of an instrument for producing a steady flow of liquid.

3.2. The flow investigated was produced in a wooden trough 364 cm. long, 10·2 cm. wide, and 5 cm. deep, all measurements being internal. The upper end was closed and the lower open, and the whole was painted. The heights of the ends of the trough above the bed could be adjusted by means of blocks. The water-supply was taken from a tank designed to maintain a constant head, and before it entered the trough it was made to pass through Mr. Mallock's device for reducing irregularities of flow. In this it first percolated through a number of holes in a brass plate and then ran over two weirs and finally down a smooth metal ledge into the head of the trough. Except at the very lowest speeds, when it was difficult to keep the whole of the ledge wet, the water entered the trough in a uniform thin sheet whose width was nearly that of the channel.

To determine ν or κ it was necessary to measure two of the three quantities Q, u_1, and ζ. The first offered no difficulty; it was sufficient to measure the total rate of supply of water by observing the time needed to fill a 2000 c.c. measuring jar, and then to obtain Q by dividing the flow per second by the breadth of the trough. The depth of the water was much more difficult to find. Had the surface been actually a plane, it might have been done by placing a bar of square section across the top of the trough and then measuring down to the bottom and to the free surface by means of a steel scale. The surface, however, was always covered with waves. The most conspicuous were standing waves, spreading like ship-waves from places at the edges where the film raised by surface tension had dried. These could be considerably reduced for a short time by running the hand along and re-wetting the sides. In addition there were usually progressive waves, apparently of greater amplitude, but more difficult to see on account of their speed. On account of the two types of waves, it was impossible to be confident that measures of the depth could be trusted within a millimetre; since the total depth was usually only about 5 mm., and since it would have to be cubed in the calculation, this method was abandoned. Hopf comments on the difficulty of measuring the depth, but seems to have succeeded better than I did.

I therefore resorted to measuring u_1 by observing the time it took a recognizable object to pass through a known distance. At first, pieces of paper about 1 cm.^{2} in area were dropped in at 50 cm. from the head of the trough and timed over the remaining 314 cm. This method usually worked well, except when the depth was small, when the paper was liable to drag on the bottom; it was easy to see when this was happening, but it led to the rejection of a considerable number of observations. It proved to be more convenient to observe a drop of ink; the front of a patch of ink gave a measure of the velocity at the surface which agreed satisfactorily with the results found with paper.

The critical Reynolds number, corresponding to the lowest value of Q that makes the flow turbulent, was found by dropping ink into the water. In viscous flow the ink was drawn out into a thin line, save for a faint uniformly tinted patch left on the surface, probably by some surface tension effect. In turbulent flow the front of the inky patch was speckled, not uniform, but shaded behind into a long region where the tint seemed to vary continuously. The ink used was for the most part a blue-black fountain-pen ink. Its density was considerably greater than that of water. A red ink, made up to the density of water by the addition of a little methylated spirit, was also used, but showed no systematic difference; probably in both cases the mixing when the ink was added was sufficiently thorough for the difference of density to be unimportant.

It was important that the length of the trough should be along the lines of steepest slope of the bottom; in other words, that lines of the bottom perpendicular to the sides should be level. Otherwise the water flowed down one side, and too low results were obtained for the viscosity or the skin friction coefficient.

If Q and u_1 are observed, we can calculate ν or $m\kappa$ from the formulæ

$$m\kappa = Qg \sin \alpha / u_1^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\nu = \frac{9}{8} \frac{Q^2 g \sin \alpha}{u_1^3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The results in the table are arranged in order of ascending values of Q; $m\kappa$ and ν have been calculated separately for each set of observations.

It is seen that the first three values of ν found from the experiment are approximately equal to the true viscosity of water. The correct values found from the tables for water at the actual temperatures are 0·0131, 0·0119, and 0·0115. For these rates of supply the flow was therefore presumably entirely or almost entirely laminar. For all other values of Q, however, the value of ν found from formula (2) was much greater than the true viscosity; the motion was therefore turbulent. Omitting then the first three entries, we can use the remaining 21 to find $m\kappa$. The frequency distribution of the various values of 1000 $m\kappa$ is as follows:—1·7 to 1·9, 2; 1·9 to 2·1, 2; 2·1 to 2·3, 6; 2·3 to 2·5, 3; 2·5 to 2·7, 3; 2·7 to 2·9, 4; 2·9 or more, 1. The arithmetic mean is 2·38, and the standard deviation 0·31. Hence the probable error of the arithmetic mean is 0·05. Thus the product $m\kappa$ is 0·00238 ± 0·00005.

Q. cm.^{2}/sec.	u_1. cm.^{4}/sec.	cosec α.	ν. 10^{-2} cm.^{2}/sec.×.	$m\kappa$. 10^{-3}×.	n.
2·97	32·9	22·3	1·20	3·68	
3·46	37·5	24·3	1·03	2·65	
4·29	45	22·2	1·01	2·08	
6·35	50	22·3	1·60	2·24	
7·35	68	12·3	1·54	1·87	
7·46	53	24·3	1·66	1·99	
7·60	58	22·3	1·75	2·05	
12·6	48	43	3·68	2·60	
12·6	73	12·3	......	2·58	
13·7	60	24·3	......	2·57	0·87
16·4	68	22·3	......	2·28	0·77
17·8	65	22·3	......	2·87	0·75
18·6	67	22·2	......	2·73	0·84
18·9	87	12·3	......	2·28	
18·9	95	7·9	......	2·75	0·81
18·9	70	23·0	......	2·33	
22·2	71	22·2	......	2·75	0·88
26·7	79	22·2	......	2·38	0·82
31·3	85	22·2	......	2·26	0·87
37·6	83	22·3	......	2·90	
40	131	7·35	......	2·38	
40	106	15·6	......	2·12	
40	61	69	......	1·74	
40	103	15·6	......	2·30	

The chief factor in producing the deviations from the mean value is the inaccuracy of the velocity. The observed time of transit of the water along the trough was on an average about five seconds. It was measured with a stop-watch graduated to fifths of a second. Each reading was repeated several times, and as a rule the observations differed among themselves by one or two fifths of a second. Thus the probable error of the velocity is comparable with 4 per cent. It is cubed in the calculation, giving an error of 12 per cent. in $m\kappa$. This is nearly equal to the standard deviation of the determinations. Q and α can hardly be in error by more than 1 or 2 per cent. A more accurate way of determining the velocity may therefore lead to a considerable reduction in the outstanding probable error.

3.3. *Determination of m.*—When the velocity was found by means of ink drops, the front and the back of the inky patch in the water were, as a rule, both timed along the trough. It seems reasonable to suppose that eddies distributed the ink vertically throughout the turbulent layer. If any ink entered the non-turbulent layer, however, it would be extended so rapidly lengthwise as to become very much fainter than the ink in the turbulent layer. Hence in turbulent motion the back of the inky patch would be expected to correspond to the velocity at the transition between the turbulent and non-turbulent layers. On this assumption, the value of n is given in the table. The mean value is $0{\cdot}83 \pm 0{\cdot}02$. Hence, by 2.2 (10), m is $0{\cdot}94 \pm 0{\cdot}01$. Thus κ is $0{\cdot}00253 \pm 0{\cdot}00006$.

3.4. *The critical Reynolds number.*—With the trough at inclinations of 1/15 and 1/23, drops of ink were added to find out whether the motion was in fact turbulent or not; in each case it was found that turbulence set in when Q was about 3·8 cm.^{2}/sec. The temperature was 12°·4, making the viscosity 0·0123 cm.^{2}/sec. Thus the critical Reynolds number was about 310.

Hopf gets 300 to 330 by a different method. He finds ν by a formula equivalent to 3.2 (2). It remains constant for values of Q up to a certain limit, and then begins to increase nearly linearly with Q. This limit is taken to give the critical Reynolds number.

Up to this value the motion is purely viscous, and the mean velocity is 2/3 of the surface velocity. Above it, the vertical extent of the turbulent region generally increases and the ratio at the same time rises.

It was seen in 2.3 that the two laws of fluid friction became equivalent when the Reynolds number was $4/3\kappa$, which we now find to be 530. There must therefore be a gradual transition from one law to the other, not a sudden change from a linear law to a square law when Q/ν reaches 310.

3.5. *The eddy viscosity.*—If we use 2.3 (11), with the values found for n and κ, we have in general

$$k = 0{\cdot}0080\,Q. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This result depends only on the hypotheses that the supply of fluid is much above the critical Reynolds value and that k is the same at all distances below the surface. It might vary on account of variation in n, but such variation seems unlikely to be great. If it occurred it would probably act in the direction of making the top more independent of the bottom at the higher speeds; thus n might diminish. Even, however, if n became zero, k would only change to $\frac{3}{4}\kappa Q$ or $0{\cdot}00192\,Q$. The order of magnitude of k therefore seems to be fixed in any case. With the largest value of Q used in these experiments, namely 40 cm.^{2}/sec., k is found to be 0·32 cm.^{2}/sec.

3.6. *The non-turbulent layer.*—When the rate of flow was only two or three times the critical rate, a drop of ink placed in the stream penetrated into the turbulent layer and was drawn out into a long straight filament by the shearing in that layer. The ink that stayed in the turbulent layer naturally became diffuse and rushed ahead. With greater rates of flow the non-turbulent layer became thinner, and it became more difficult to make it visible. Merely injecting ink into the stream in the neighbourhood of the bottom did not produce the desired effect. Probably the action of forcing ink into the water in itself introduced a certain amount of turbulence locally, and the turbulent fluid immediately mixed with the turbulent layer and was carried away. When a larger amount of ink, say 0·5 c.c., was projected nearly normally at the bottom, more success was obtained. A little of it in this case became entangled in the non-turbulent layer. With the highest values of Q and α used, corresponding to a velocity of over a metre a second, some ink injected in this way could be seen several seconds afterwards, advancing in a stream-line motion with a velocity about 1 per cent. of that at the surface.

4. COMPARISON WITH RELATED RESULTS.

The value found for the coefficient of skin friction, namely 0·00256, may be compared with those found by G. I. Taylor[*] from observations of wind at various heights, namely 0·0023 for light, 0·0032 for moderate, and 0·0022 for strong winds. The two problems refer to somewhat different conditions, however. In the air there is an almost permanent tendency to stability, owing to the difference between the actual and the adiabatic lapse-rates of temperature with height; this is absent from the present problem. Further, my formula expresses the skin friction in terms of the velocity of the water at the free surface; Taylor's expresses it in terms of the velocity at the lowest level recorded by a pilot balloon, whereas the meteorological analogue of the velocity at the free surface is probably the geostrophic wind. Thus the numerical agreement between my coefficient and Taylor's, beyond the order of magnitude, is accidental.

In work on tidal friction in shallow seas, Taylor and I took the coefficient of skin friction in tidal currents to be 0·002, the surface velocity being used as the datum; the results of this paper indicate a coefficient about 25 per cent. greater.

In hydraulics, computations for conduits are usually based on the Chézy formula, which in the notation used here is equivalent to

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[*] Proc. Roy. Soc. A, xcii. pp. 196–199 (1916).

$$mu_1 = C(\zeta \sin \alpha)^{\frac{1}{2}},$$

C being the Chézy coefficient. Comparing with 2.2 (1), we have

$$\kappa = m^2 g/C^2.$$

The Chézy coefficient in metre-second units, with an unplaned plank bottom, when the water is shallow in comparison with its width, is about 55 *. With this value, and our value of m, we find that κ is 0·00286. For a neat cement bottom C is 64, making κ equal to 0·00221. It may be remarked, however, that the smallest depth given in the table quoted corresponds to a value of Q of 880 cm.^{2}/sec., whereas those in my experiments ranged from about 3 to 40 cm.^{2}/sec. On the other hand, much experimental evidence is harmonized if we suppose that κ is really proportional † to $(\nu/Q)^{\frac{1}{4}}$, so that a value of κ of 0·0022, for Q equal to 880 cm.^{2}/sec., would correspond to one of 0·0045, for Q equal to 40 cm.^{2}/sec. In that case my lower values will have to be attributed either to the greater smoothness of the bottom or to a departure of friction for moderate values of Q from the law appropriate to large values.

Merriman, who follows Bazin, quotes higher values of C for greater depths, but this is probably due in part to edge effects. On the other hand, lower values of C, ranging down to 17, are given for other types of bottom, the lowest referring to weeds. The theory of the effect on the skin friction of variations in the nature of the bottom is likely to be rather difficult. So long as the projections on the bottom are small compared with the thickness of the non-turbulent layer, and so long as the fluid wets the bottom, it seems unlikely that they can affect the friction appreciably. A slight confirmation of this may be afforded by the fact that Hopf's determinations of the critical value of Q/ν for water flowing over brass and glass agree with mine for a planed plank bottom. If the projections are great enough to penetrate the non-turbulent layer, however, they may affect the character of the turbulence: the projections, by obstructing the current, may considerably increase the friction. Incidentally, as v. Kármán points out, they improve the accuracy of the proportionality of the friction to the square of the velocity. Weeds differ from other projections in being movable. Among the weeds the flow may be largely viscous, especially if they are growing thickly; thus they may much reduce the effective depth of the stream. It seems likely that the ratios of the height of the projections to the depth of the fluid and the thickness of the non-turbulent layer are important data relative to the law of friction in a stream.

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* Merriman, 'Treatise on Hydraulics,' p. 314.

† *Cf.* T. von Kármán, *Zs. f. ange. Math. u. Mech.* i. pp. 233–252 (1921).

In the flow of fluids in pipes turbulence usually develops when u_0a/ν reaches 1015: here u_0 is the mean velocity and a the radius. In the rectangular case, Q was practically the ratio of the rate of flow through a section to the wetted perimeter of the section; in a circular pipe this is $\frac{1}{2}u_0a$. Thus the critical value of the analogue of Q/ν is 525, instead of 310 as found for the trough. The difference may be attributed to the additional possibilities of instability introduced by the free surface. Streams in turbulent flow, however slight the wind may be, never seem to have perfectly even surfaces; the surface is always quivering, and reflects irregularly. The skin friction in pipes is about $0{\cdot}0025\,\rho u_0^2$ per unit area; if it is expressed in terms of the maximum velocity, the numerical coefficient will have to be less than in the case of a stream with a free surface.

5. PROGRESSIVE WAVES.—Reference has already been made to the presence of progressive waves on the water during the experiments. It was actually to test a theory of the formation of such waves that the experiments were originally undertaken. It has been noticed by Vaughan Cornish[*] that the water in certain Alpine conduits, with plane bottoms and rectangular sections, does not flow in a steady stream but in a series of waves. The height of the waves is comparable with the mean depth of the water (about 3 inches), and the velocity is appreciably greater than that of the surface of the water. It appeared possible that the development of waves of such size might be due to an essential instability of the uniform flow of a stream in certain conditions, and on investigation it is found that such instability is present in all cases when the slope of the bottom exceeds a certain definite numerical value. It is to be noticed that this instability is different in character from the instability that leads to the transition from laminar flow to turbulent flow. It presupposes that the flow is already turbulent, and indicates a transition, from the ordinary flow of a stream with a plane or nearly plane

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[*] 'Waves of the Sea and other Water-Waves,' pp. 294–330 (1910).

free surface, to a different turbulent flow with the surface marked by moving transverse ridges.

In the following theory the motion will be supposed thoroughly turbulent, the friction proportional to the square of the velocity, and the wave-length of the disturbance of the steady motion long compared with the depth of the fluid. As an approximation, the velocity u will be supposed the same at all depths. The equation of continuity is

$$\frac{\partial\zeta}{\partial t} = -\frac{\partial}{\partial x}(u\zeta). \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The dynamical equation is obtained by integrating the equation of motion down the slope with respect to the depth, the range of integration being from the bottom to the free surface. It is

$$\zeta\left(\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x}\right) = \left(g\sin\alpha - g\cos\alpha\frac{\partial\zeta}{\partial x}\right)\zeta - \kappa u^2. \quad . \quad (2)$$

In steady motion, let

$$\zeta = h, \quad u = \mathrm{U}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and in the disturbed motion let

$$\zeta = h + \zeta', \quad u = \mathrm{U} + u'. \quad . \quad . \quad . \quad . \quad (4)$$

We have the steady motion condition :

$$gh\sin\alpha = \kappa\mathrm{U}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If for shortness we write σ for $\partial/\partial t$, and p for $\partial/\partial x$, equations (1) and (2) reduce to

$$(\sigma + \mathrm{U}p)\zeta' = -hpu', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$(\sigma + \mathrm{U}p)u' = \left(\frac{g}{h}\sin\alpha - gp\cos\alpha\right)\zeta' - \frac{2\kappa\mathrm{U}}{h}u', \quad . \quad . \quad (7)$$

where all terms depending on squares and products of the departure from steady motion have been neglected. On eliminating and using (5), we find that u' and ζ' are both annulled by the operator

$$(\sigma + \mathrm{U}p)^2 + \frac{2\kappa\mathrm{U}\sigma}{h} + 3gp\sin\alpha - ghp^2\cos\alpha. \quad . \quad . \quad (8)$$

Any small disturbance of the steady state that may exist at first can be expressed as a combination of sines and cosines of multiples of x, or alternatively as a combination of terms of the form $e^{\iota\beta x}$, where β is purely real. Then each term of this latter type will give solutions of (8) of the form $Ae^{\gamma t+\iota\beta x}$, where A and γ are constants. A depends wholly on the initial conditions; γ is to be found by writing $\iota\beta$ for p and γ for σ in (8), equating the resulting expression to zero, and solving for γ. If the resulting value of γ has a zero or negative real part, the steady motion is stable; but if it has a positive real part, any initial small disturbance of the type considered will increase exponentially until its amplitude becomes so great that its square can no longer be neglected. We actually find on solving that

$$\gamma = -\mathrm{U}\iota\beta - \frac{\kappa \mathrm{U}}{h} \pm \left(\frac{g}{h}\right)^{\frac{1}{2}} (\kappa \sin\alpha - \iota\beta h \sin\alpha - \beta^2 h^2 \cos\alpha)^{\frac{1}{2}}. \quad (9)$$

Put

$$\beta h = \lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

so that λ is a pure number. Then

$$\beta \mathrm{U} = \lambda\left(\frac{g \sin\alpha}{\kappa h}\right)^{\frac{1}{2}}; \quad \frac{\kappa \mathrm{U}}{h} = \left(\frac{\kappa g \sin\alpha}{h}\right)^{\frac{1}{2}}; \quad . \quad (11)$$

and

$$\gamma = \left(\frac{g \sin\alpha}{\kappa h}\right)^{\frac{1}{2}} \left[-\iota\lambda - \kappa \pm (\kappa^2 - \iota\kappa\lambda - \kappa\lambda^2 \cot\alpha)^{\frac{1}{2}}\right]. \quad (12)$$

It is clear from this result that, for any value of β, at least one of the associated values of γ has a negative real part; further, that if α is small enough they both have negative real parts. This corresponds to the ordinary fact of observation that waves on a stream of small slope tend to die out. The transition to instability can occur only if γ passes through a value with a zero real part. But the condition for γ to be purely imaginary is that the square root in (12) shall be of the form $\kappa+\iota\delta$, where δ is real. Expressing this equality, we derive the equation:

$$\kappa^2 - \iota\kappa\lambda - \kappa\lambda^2 \cot\alpha = \kappa^2 + 2\iota\kappa\delta - \delta^2. \quad . \quad . \quad . \quad (13)$$

Equating real and imaginary parts we have

$$\delta = -\tfrac{1}{2}\lambda; \quad \delta^2 = \kappa\lambda^2 \cot\alpha; \quad . \quad . \quad . \quad . \quad (14)$$

and on eliminating δ we have simply

$$\tan\alpha = 4\kappa. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Thus the steady flow will first become unstable when the slope is just greater than 4κ, or practically 1 in 100. For the first wave that is able to grow, γ has imaginary part $\left(\frac{g \sin\alpha}{\kappa h}\right)^{\frac{1}{2}}(-\frac{3}{2}\iota\lambda)$. The velocity of the wave is therefore down stream and equal to $-\gamma/\beta$, or $\frac{3}{2}$U. The wave therefore travels one and a half times as fast as the water. The instability develops at the same stage for all wave-lengths, subject to the condition of the problem that the wave-length is great compared with the depth of the water.

It may be remarked that if the slope has the critical value 4κ, the velocity of the water is just equal to $2(gh)^{\frac{1}{2}}$, and the velocity of the wave will exceed that of the water by $(gh)^{\frac{1}{2}}$, which is just the velocity of a long wave in standing water. Cornish comments on the fact that the waves in his conduits seemed to gain on the water with a velocity equal to that of a wave in standing water of the same depth; it appears that the present argument is able to account for this fact, at any rate at the beginning of the formation of waves.

When waves have once begun to form, it is clear that the water of the crests will tend to rush down, gaining over the troughs, till the surface has been converted into a series of bores following one another down stream. A considerable extension of the theory would be required to give a quantitative account of the final stage. The theory as here developed deals only with the earliest stage of the development of roll-waves, and shows that they are to be expected in all rectangular conduits whose slopes exceed 1 in 100. Those described by Cornish have slopes of 1 in 14 and 1 in 22 respectively. There seems no reason why similar instability should not give rise to roll-waves when the bottom of the conduit is not plane, but has a curved section, so long as the section is uniform. If, however, the bottom is irregular, waves produced in this way will be deflected transversely and have their velocities changed at irregular intervals by the projections on the bed; hence they will only add to the general appearance of turbulence at the surface, without producing any characteristic roll-wave. It is presumably for this reason that regular roll-waves are not in general observable in mountain torrents.

I attempted to investigate the properties of travelling waves in the trough, but no definite results were obtained. It was clear that their velocity was distinctly greater than that of the water. They were timed over a measured distance to determine the velocity, but the results were not sufficiently accurate to give a definite test of any theory. They were consistent with the velocity of the waves relative to the water being either half the velocity of the water or the velocity of waves in standing water of the same depth; it proved impossible to discriminate between these two values. In the trough, of course, the waves did not grow to their full magnitude; their amplitude probably never exceeded a millimetre (and if it had done so, the determinations of the coefficient of skin friction made in this paper would have been vitiated). This fact is to be attributed to the shortness of the trough. Cornish remarks that in the Grünnbach the roll-waves were not completely formed when the water had been travelling along the conduit for 465 feet, the mean depth being about 3 inches. Thus for a mean depth of 5 mm. the water would have to travel 30 feet, about three times the length of my trough, before even this stage of development was reached.

SUMMARY.

Observations have been made of the flow of water in an inclined trough of rectangular section, with a planed wood bottom. Defining the Reynolds criterion for such a system as Q/ν, where Q is the total volume flux of water per unit breadth per unit time, and ν is the kinematic viscosity, it is found that turbulence first develops when the Reynolds number is about 310, distinctly less than the corresponding number for a pipe. When the Reynolds number is between 2 and 13 times the critical value, the observations are consistent with the skin friction coefficient κ being $0{\cdot}00253 \pm 0{\cdot}00006$, where the frictional force per unit area of the bottom is supposed to be $\kappa\rho u_1^2$, u_1 being the surface velocity. The mean velocity is about 0·94 of the surface velocity. The existence of a layer of water in laminar motion at the bottom of the trough was verified even at the highest velocities tested. The above interpretations have been put on the experimental results on the supposition that a uniform eddy viscosity exists at all depths between the free surface and the non-turbulent layer; on the same hypothesis it appears that the eddy viscosity must be equal to $0{\cdot}0080\, Q$.

A theory has been constructed to account for certain travelling waves observed by Vaughan Cornish in steeply-inclined conduits. It appears that the uniform turbulent flow of a stream, with a plane free surface, becomes unstable when the mean slope exceeds 1 in 100, and that it is then replaced by a series of bores travelling faster than the water. Observational evidence is qualitatively consistent with the theory, but quantitatively several points remain to be tested.

LXXXV. *Wind-Channels in Aerodynamics.* *By* N. K. Bose, *Ph.D.* (*Göttingen*), *Reader in Mathematics, Aligarh Moslem University, India* *.

FOR experiments on aeroplanes and its parts, to determine the air resistances of tails and struts, the head and the fuselage, to calculate the lift and the drag, the angle of attack of wings, wind-channels have come to occupy a unique position. In fact, they offer the safest and, under certain circumstances, the most accurate method for determining the aerodynamical characteristics of an aeroplane. The only other accurate and reliable method is that in which aeronauts test their planes as to their reliability, controllability, and stability while they are in actual flight. This method, in so far as it affords a first-hand information, is of the utmost importance, but the amount of risk involved of danger to life and person prohibits its indiscriminate use. To minimize these difficulties and danger, to declare a plane safe for all practical purposes, experiments in wind-channels are now the only means at our disposal. Of course, the usefulness of wind-channels is limited by considerations of scale-effect in models and turbulences in air. Of recent years, Prandtl and Eiffel have shown that, if we could arrange the dimensions and velocities of the model experiments and of actual flights so that in both the cases Reynolds' number remains constant, scale-effect can be eliminated. This important discovery has extended the utility of wind-channel experiment to all those cases that are of any importance in aeronautics.

In wind-channel experiments, as is well known, the body to be experimented upon is placed in the channel through which a steady current of air is blown or drawn. By various means this current of air is rendered free from eddies, and the six components of forces on the body are measured. The quantities that concern wing-measurement most are its lift and drag for different angles of attack and the corresponding positions of the centre of wind-pressure, but these quantities measured in the channel are quite different from the corresponding quantities when measured in free space. We know that the stream-line generated by a body which is moving in a medium or over which the medium is passing whose boundaries extend to infinity, would be quite distinct from those in a limited medium. This fact of hydrodynamics will have to be taken into account in assigning any particular angle of attack to lift and drag coefficients, Ca, Cw. In any wind-channel experiment with wings, what is usually done is that the wing is set at a particular angle of attack (that is, the angle between the chord of the wing and the direction of the wind, which is usually horizontal, measured) and its corresponding lift and drag are then experimentally determined. But this geometrically measured angle of attack, it will be seen, is not the same as the real or effective angle of attack. By effective angle of attack is meant that angle which the real stream-lines make wlth the chord of the wing.

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* Communicated by the Author.

At first, let us consider the case of a plane or a wing of limited dimensions placed in a medium of unlimited extent flowing steadily in a direction, say, horizontal. This will call forth a vertically downward disturbance in the medium (disturbances in other directions we are not at present concerned with) which is mechanically known as downwash. This downwash of a wing, as is apparent, will modify its own lift capacity—*i. e.*, its angle of attack will be diminished by the amount $\tan^{-1}\frac{w_0}{V}$, where w_0 is the downwash velocity on the wing and V the velocity of the free stream at infinity. We know that the lift and the angle of attack of a wing are connected by the following simple relation when the angle of attack is small:

$$A = \mathrm{CaFq} \quad \text{and} \quad \mathrm{Ca} = 2\pi(\alpha_\infty + \beta),$$

where A is the lift and Ca the lift-coefficient, F the area of the wing, $q = \frac{1}{2}\rho V^2$, α_∞ is the angle of attack of a wing of infinite lateral extents, and β is the angle which the sectional arc of the wing subtends at its centre (when the radius of curvature of the wing is very great). It has been found by experiment that Ca and α are linearly connected, and theory gives for wings of circular section

$$\mathrm{Ca} = 2\pi(\alpha_\infty + \beta)$$

per unit breadth, and

$$\sin \beta/2 = t/R_1,$$

where $2t$ is the sectional chord and R_1 the radius of the earth. Now this angle of attack α_∞, which is called the angle of attack for a wing of unlimited length, cannot be found directly from experiment, as when the plane is of unlimited length the downwash is absent, so that the angle between the chord of the aeroplane section and the direction of flow of air current gives the angle of attack; but when we have to deal with a finite length of the plane, this downwash comes in, so that what is the real direction of the current at infinity is no longer the real direction in which the air current strikes the chord of the plane, and the geometrical angle of attack is consequently not the real or effective angle of attack of the aeroplane. So in the case of a monoplane, when we have got to calculate the lift from the geometrical angle of attack we have to transform the geometrical angle which is measured from experiment to the effective angle of attack at which the wind really strikes the chord. This formula for transformation for a monoplane is

$$\alpha_\infty = \alpha - \tan^{-1}\frac{w_0}{V},$$

as we can easily see that the downwash gives the free stream velocity V a downward component, w_0, and the resultant goes at an angle $\tan^{-1}\frac{w_0}{V}$ to the direction of V, so that the geometrical angle of attack is diminished by this amount.

So far we have not considered the influence of the channel. This influence of the channel, it will be broadly seen, will be to introduce a further modification in the angle of attack. The disturbances due to the channel will consist in superimposing another downwash, called induced downwash w_0', and in giving a curvature to the stream-lines given by

$$\frac{1}{R} = \frac{\partial}{\partial y} \cdot \tan^{-1}\frac{w_0'}{V} = \frac{1}{V}\frac{\partial w_0'}{\partial y} = \frac{1}{V}\left(\frac{\partial w'}{\partial y}\right)_0,$$

if w_0' is small in comparison with V, where y is measured along the stream and the curvature is taken in a vertical plane of a stream-line as it crosses the vertical plane of the wind.

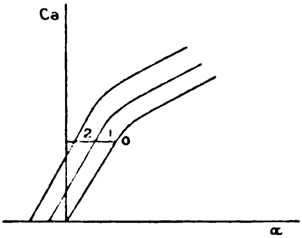
The effect of this induced downwash is apparent, and the change in the angle of attack will be $\tan^{-1}\frac{w_0'}{V}$. Hence, when only the two downwashes are considered

$$\alpha_\infty = \alpha - \tan^{-1}\frac{w_0}{V} - \tan^{-1}\frac{w_0'}{V}.$$

The effect of the induced curvature will be somewhat complicated and must be considered in detail.

Suppose we have three planes, 0, 1, 2, of which 0 has got no curvature, 1 has a curvature $1/R_1$, and 2, $1/R_2$. It has been found from experiment that the relation between Ca, the lift-coefficient, and α, the angle of attack, is given by the accompanying figure for 0, 1, 2. Then it is apparent that 2 has a smaller angle of attack than 1, and 1 smaller than 0 for the same lift-coefficient Ca. This fact can be theoretically expressed by the relation

Fig. 1.



$$A = 2\pi\rho t V^2 \sin(\alpha+\beta/4),$$

where ρ is the density of the medium. If f be the height of the middle point of the arc above the chord,

$$\frac{f}{t} = \tan\beta/4 \quad\text{and}\quad R_1=\frac{f^2+t^2}{2f},$$

$$\text{or}\quad 1/R_1 = 2f/(t^2+f^2),$$

$$t/R_1 = 2f/t = \beta/2.$$

$$\therefore\quad Ca = 2\pi\sin(\alpha+\beta/4)/\cos\beta/4$$

$$= 2\pi(\alpha+\beta/4) = 2\pi(\alpha+t/2R_1).$$

From this it is apparent that, if we want to have the same lift-coefficient, Ca, for the three planes, the angle of attack must be diminished by amounts $t/2R_1$ for 1 and $t/2R_2$ for 2, where t is half the breadth of the plane and $1/R$ is the curvature of the surface of the plane.

Thus, when the stream-lines are straight the effect of the curvature of the plane is to diminish the angle of attack for the same lift-coefficient by $t/2R$.

If now we want to find the effect of a curvature in the stream-lines on a plane which has got also curvature of its own, then if $1/R$ be the curvature of the stream-lines and $1/R_1$ that of the plane, the effective curvature of the plane in this case is only $1/R_1 - 1/R$. By effective curvature we mean the curvature of the plane which is effective in bringing about a diminution of the angle of attack. So in this case when a curved plane finds itself in a stream whose stream-lines have got a curvature of their own, to have the same lift-coefficient Ca as it had when the stream was straight, the angle of attack must be diminished by $\frac{t}{2}\left(\frac{1}{R_1}-\frac{1}{R}\right)$. So the geometrical angle of attack must be diminished by

$$\frac{t}{2R_1}-\frac{t}{2}\left(\frac{1}{R_1}-\frac{1}{R}\right)=\frac{t}{2R}.$$

Hence the effective angle of attack of a wing in a wind-channel whose geometrical angle of attack is measured is given by

$$\alpha_{\infty}=\alpha-\tan^{-1}\frac{w_0}{V}-\tan^{-1}\frac{w_0'}{V}-\frac{t}{2R}.$$

Generally w_0 and w_0' are comparatively small in comparison with V. Hence

$$\alpha_{\infty}=\alpha-\frac{w_0}{V}-\frac{w_0'}{V}-\frac{t}{2R}.$$

Thus the problem of a wind-channel resolves itself into finding w_0, w_0', and $1/R$, *i.e.*, the two downwashes and curvature of the stream-lines. For our present purpose we want all these quantities on the wing itself.

To find the influence of a wing on the surrounding medium reference must be made to a former paper of mine in this Magazine (*vide* Phil. Mag. xlviii. p 113, July 1924). There the aeroplane surface or wing surface has been divided into so many differential surfaces, so that each small elemental surface may be looked upon as an aeroplane on which fluid pressure is calculated independently of all other elements, and then it is integrated throughout the whole volume occupied by these elemental aeroplanes. The conception is something like this; at each elemental aeroplane there is a circulation which is denoted by γ, and from the edges of this element vortices flow off with the fluid; the strength of the elemental vortices is ϵ. So we can picture a thing like this: under each differential aeroplane there is a vortex of strength γ which is fixed with the element, and from each element a vortex line is flowing off with the liquid whose strength per unit volume is ϵ, so that the aeroplane becomes the seat of innumerable fixed vortices of strength γ per unit volume, and from the aeroplane free vortices are flowing off with the liquid like ribbons with strength ϵ per unit volume.

Again it has been observed experimentally that the density of the lift of a wing (lift per unit length) is not constant over the whole length of the wing, but in general falls off gradually from a maximum at the middle to 0 at the ends. In accordance with what has been proved there corresponds to this a circulation decreasing from within outwards. Therefore, according to the theorem that by the displacement of a closed curve round the wing the circulation Γ can only change if a corresponding quantity of vortex filament proceed off from the trailing edge, wherever Γ changes a vortex filament will flow off with the liquid, and as Γ changes from point to point of the wing these filaments flow off from every point of the wing. Here a special arrangement of the vortex filament will help us in our mathematical treatment. We suppose that a vortex filament of strength $\Gamma(x)$, with a right-handed screw rotation, coming from infinity behind the plane meets the lifting line (the single line vortex which replaces all the bound vortices and passes through the C. G. of the vortices) at a distance x from the middle of the wing measured to the right of the pilot. This filament then turns towards the right forming a part of the lifting line, goes a short distance dx along it, and then again turning to the right goes to infinity parallel to the incoming filament. Then another filament of strength $\Gamma+d\Gamma$ travelling from infinity in the same plane as the former filament pair meets the lifting line at $x+dx$ and behaves as the former one did. Thus we see that at every point of the lifting line a filament of strength Γ goes out and one of strength $\Gamma+d\Gamma$ comes in, so that at every point of the lifting line a vortex filament of strength $d\Gamma$ will be coming in and the lifting line will be a vortex line of strength $\int d\Gamma = \Gamma$. With this arrangement of the vortices we are now in a position to remove the wing and consider its effect on the surrounding medium by replacing it by this vortex arrangement.

The law according to which the lift or the circulation Γ varies with x, *i.e.* with the distance from the middle of the plane, is fairly well known. It is evident that it depends on the aspect-ratio and the perspective of the plane. A remarkable distribution of circulation was found in the form

$$\Gamma = \Gamma_0\sqrt{1-\frac{x^2}{l^2}},$$

where Γ_0 is the circulation at the middle and l the half-span of the wing. This distribution is called Elliptic Distribution of Lift, and has a peculiar property of giving to a monoplane the smallest drag that is possible for it with the total lift, the span, and the velocity given. Another characteristic in its favour is that all distributions that have as yet been observed deviate but slightly from this, so that any conclusion drawn from the assumption of elliptic distribution will not go very wide of the mark. Another outstanding feature of this distribution is that it gives a constant downwash velocity over the whole span of the wing ; it is given by

$$w_0 = \frac{\Gamma_0}{4l},$$

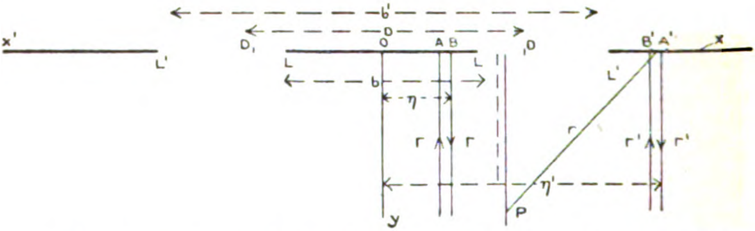
and for this distribution

$$A = \tfrac{1}{2}\pi\rho V l \,.\, \Gamma_0,$$

$$\therefore \quad w_0 = \frac{A}{2\pi\rho V l^2}.$$

When this vortex system is placed in a medium which is bounded by the walls of a wind-channel, we know that the boundary (which is assumed circular here) may be removed and its effect calculated by replacing it by the images of the vortices at the inverse points. The accompanying figure will make it clear.

Fig. 2.



The above figure is in the plane of the vortices which is horizontal, LOL is the wing, O its middle point, D and D are the points of section with the canal, L′ is the inverse point to L with respect to the circle, the inverse vortices extend to infinity along L′X and L′X′, OY is horizontal and taken along the direction of the stream. One vortex Γ enters LOL at A $(x, 0)$ and goes out at $(x+dx, 0)$, the inverse point B′ also possesses a vortex Γ′ coming in and at A′ going out. We have

$$\Gamma = \Gamma_0 \surd(1-4\eta^2/b)$$

$$\Gamma' = \Gamma_0 \surd(1-4\eta^2/b^2) = \Gamma_0 \surd(1-b'^2/4\eta'^2),$$

where

$$b = 2l, \quad b' = \mathrm{L'OL'}.$$

w_1 = vertical component of the velocity induced by the vortex at B′ at P (x, y)

$$= -\frac{\Gamma'}{4\pi(\eta'-x)}\left(1+\frac{y}{r}\right).$$

The pair of vortices at B′ and A′ having the same strength Γ′ but different rotation, produces then a vertical velocity at P which can be written as the difference of the effects of the two vortices at A′ and B′ which are closed together:

$$dw_1=\frac{\partial w_1}{\partial\eta'}d\eta'=\frac{\Gamma'}{4\pi}\left[\frac{1}{(\eta'-x)^2}\left(1+\frac{y}{r}\right)+\frac{1}{\eta'-x}\cdot\frac{y}{r^2}\cdot\frac{\partial r}{\partial\eta'}\right]d\eta'$$

$$=\frac{\Gamma'}{4\pi}\left[\frac{1}{(\eta'-x)^2}\left(1+\frac{y}{r}\right)+\frac{y}{r^3}\right]d\eta'.$$

Due to the cross-vortex B′A′,

$$dw_2=\frac{\Gamma' d\eta'}{4\pi}\cdot\frac{y}{r^3}.$$

Hence the whole downward induced velocity at P due to the bound and the free vortices at B′ and A′

$$dw'=\frac{\Gamma' d\eta'}{4\pi}\left[\frac{1}{(\eta'-x^2)}\left(1+\frac{y}{r}\right)+\frac{2y}{r^3}\right]d\eta'.$$

$$\therefore\quad w'=\frac{\Gamma_0}{4\pi}\int_{b'/2}^{-b'/2}\left[\frac{1}{(\eta'-x)^2}\left(1+\frac{y}{r}\right)+\frac{2y}{r^3}\right]\sqrt{\left(1-\frac{b'^2}{4\eta'^2}\right)}d\eta',$$

$$w_0'=\frac{\Gamma_0}{4\pi}\int_{b'/2}^{-b'/2}\frac{\sqrt{1-b'^2/4\eta'^2}}{(\eta'-x)^2}d\eta',$$

since $y=0$ on the wing where w_0' is taken.

Putting

$$\xi=\frac{2b}{D^2}\,.\,x=\frac{2x}{b'},\quad\text{and}\quad\frac{b'}{2}X=\eta',\quad\therefore\quad X>1.$$

Hence

$$w_0'=\frac{\Gamma_0}{4\pi}\int_1^{-1}\frac{\sqrt{1-\frac{1}{X^2}}}{\left(\frac{b'^2}{2}X-x\right)^2}\cdot\frac{b'}{2}dX$$

$$=\frac{\Gamma_0}{2\pi b'}\int_1^{-1}\frac{\sqrt{X^2-1}}{X(X-\xi)^2}dX$$

$$=\frac{A}{\pi D^2\rho V}\left(1+\frac{3}{4}\xi^2+\frac{5}{8}\xi^4+\frac{35}{128}\xi^6+\dots\right).$$

Again

$$\left(\frac{dw'}{dy}\right)_{y=0} = \frac{3\Gamma_0}{\pi b'}\int_1^{-1}\frac{\sqrt{X^2-1}}{X(X-\xi)^3}dX$$

$$= 3\frac{dw_0'}{d\xi}$$

$$= \frac{3A}{\pi D^2\rho V}\left(\frac{3}{2}\xi + \frac{5}{2}\xi^3 + \frac{105}{64}\xi^5 + \dots\right).$$

We have put

$$\xi = \frac{2b}{D^2}x = \frac{4l}{4R^2}x = \frac{l}{R}\cdot\frac{x}{R},$$

where R is the radius of the channel. In ordinary experiment $\frac{l}{R}$ does not extend beyond 1/2 and $\frac{x}{R}$, as the point must be on the wing itself, cannot be greater than half. Hence, generally $\xi < \frac{1}{4}$ and in w_0' we need not take more than three terms, and in $\left(\frac{dw'}{dy}\right)_0$ more than two. Thus ultimately, we have

$$w_0 = \frac{A}{2\pi\rho l^2 V}$$

$$w_0' = \frac{A}{\pi\rho D^2 V}\left(1 + \frac{3}{4}\xi^2 + \frac{5}{8}\xi^4 + \dots\right),$$

and $$\frac{1}{R} = \frac{1}{V}\left(\frac{\partial w'}{\partial y}\right)_0 = \frac{3A}{\pi\rho D^2 V^2}\left(\frac{3}{2}\xi + \frac{5}{2}\xi^3 + \dots\right).$$

With these, the effective angle of attack α_∞ of a wing in a wind-channel experiment with a measured angle of attack,

$$\alpha_\infty = \alpha - \frac{A}{2\pi\rho l^2 V^2} - \frac{A}{\pi\rho D^2 V^2}\left(1 + \frac{3}{4}\xi^2 + \frac{5}{8}\xi^4\right)$$
$$- \frac{3At}{2\pi\rho D^2 V^2}\left(\frac{3}{2}\xi + \frac{5}{2}\xi^3\right),$$

where $\xi = \frac{l}{r}\cdot\frac{x}{R}$ and A, α are found experimentally.

The importance of this formula will be at once apparent, if we remember that in all wind-channel experiments it is the angle of attack which distinguishes one set of experiments from others. In the above I have not considered the influence of the breadth of the wing, as I have replaced the wing by a line vortex only. The peculiar distribution of vortices over the breadth of the wing that will satisfactorily replace it has been discussed by Dr. Birnbaum in his paper in the *Zeitschrift für angewandte Mathematik und Mechanik*, 1924. In my dissertation ("Das Doppledeckerproblem," Göttingen, 1923) I have discussed this effect in the case of a biplane, and a corresponding treatment might be done in this case. I must wait till some experimenters see how the above formula works.

In practice the average value of α_∞ over the whole span of the wing must be taken.

In the above, I have considered the case of a wind-channel in which the whole experiment is conducted in a closed place. Eiffel's method consists in experimenting in a blast of air drawn through a room, whose dimensions are large in comparison with the radius of the column of air-blast. Prandtl's improved method consists in placing a gap between two wind-channels. A current of air is drawn through the walls of a wind-channel, and then through a gap it is drawn into another wind-channel. This method combining the former two eliminates their defects. In both Prandtl's and Eiffel's methods $\Gamma' = -\Gamma$.

LXXXVI. *Longitudinal Asymmetry in the Direction of Ejection of Photo-electrons.* *By* ONA K. DE FOE, *Teaching Fellow in Physics, Washington University, Saint Louis, Missouri* *.

Introduction.

WHEN radiation falls normally upon a thin plate and ejects photo-electrons, it is observed that the number of photo-electrons proceeding from that side of the plate from which the radiation emerges (emergent side), exceeds the number of photo-electrons from that side upon which the radiation is incident (incident side). This effect appears to have been discovered by Eve[1] while attempting to show the similar natures of gamma and X-rays. Eve observed that the ionization current from the emergence side of a thin plate bombarded normally by gamma rays was not so much less than the ionization current from the incident side as the absorption of gamma rays indicated it should be for the thickness of metal used.

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* Communicated by Prof. F. W. Bubb.

[1] Eve, Phil. Mag. viii. p. 669 (1904).

In the region of gamma rays this effect has been examined by Wigger[2], Dawes[3], Mackenzie[4], and Bragg and Madsen[5]. In the region of ultra-violet light this phenomenon has been studied experimentally by Stuhlmann[6], Kleeman[7], Robinson[8], and Piersol[9]. Experiments in the X-ray region have been carried out by Beatty[10], Cooksey[11], Wilson[12], and Bubb[13].

There are two possible explanations of this effect. We may suppose, in the first place, that the velocity of the photo-electrons from the emergence side exceeds the velocity of those from the incidence side and that the number of photo-electrons from the two sides are equal. We may, on the other hand, suppose that the velocities from the two sides are equal and that the numbers are unequal.

The experimental work of Beatty[10] with X-rays and the work of Piersol[9] with ultra-violet light on this question, seem to decide in favour of the second alternative. For these observers find that the retarding potentials (and consequently the velocities) for the two sides of the plate are equal. Further light is furnished by the photographs of Wilson[12], Bubb[13], and those of the present experiment, of the tracks of photo-electrons. These photographs show definitely that the number of emergence (or forward) exceeds the number of backward photo-electrons. Furthermore, these photographs show the average range to be independent of direction.

On the theoretical side the evidence is also in favour of the supposition that the effect is due solely to the excess number of forward photo-electrons. Millikan[14] points out that, if the velocity of ejection depends on direction of ejection, Einstein's photo-electron equation

$$h(\nu-\nu_0) = mc^2(1/\sqrt{1-\beta^2}-1)$$

does not hold. For, in order to make it apply, we should have to assume that h also depends on the direction of ejection. However, h is found experimentally to be independent of the direction of ejection of the photo-electron.

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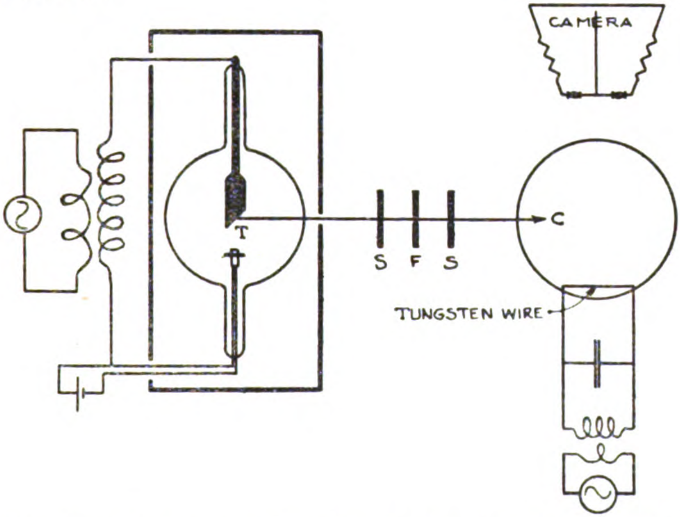
[2] Wigger, *Phys. Zeitschr.* p. 683, Oct. 26, 1905.
[3] Dawes, Phys. Rev. xx. p. 182 (1905).
[4] Mackenzie, Phil. Mag. xiv. p. 176 (1907).
[5] Bragg and Madsen, Phil. Mag. xv. p. 613 (1908).
[6] Stuhlmann, Phil. Mag. xxii. p. 854 (1911).
[7] Kleeman, 'Nature,' May 19, 1910.
[8] Robinson, Phil. Mag. xxv. p. 115 (1913).
[9] Piersol, Phys. Rev. xxiii. p. 144 (1924).
[10] Beatty, Proc. Camb. Phil. Soc. xv. p. 25.
[11] Cooksey, Phil. Mag. xxiv. p. 37 (1912).
[12] Wilson, Proc. Roy. Soc. lxxxvii. p. 277 (1912); civ. p. 1 and cv. p. 22 (1923).
[13] Bubb, Phys. Rev. xxiii. p. 137 (1924).
[14] Millikan, Phys. Rev. vii. p. 18 (1916).

There is a somewhat surprising lack, however, of definite experimental information as to the effect, on the ratio of forward to backward photo-electric current, of such obviously essential matters as the frequency of the radiation and the source of the photo-electrons. With the sole exception perhaps of Cooksey's work, all previous work possesses little more than qualitative value.

The present experiment was performed for the purpose of obtaining a definite value of the ratio of the forward to the backward photo-electric current excited in a given substance by radiation of a definite frequency.

Experimental Procedure.

In this experiment the photo-electrons were ejected from air by the K_α radiation from molybdenum. The directions of ejection of the photo-electrons were determined by taking stereoscopic pictures, by the Wilson cloud method, of the ionization tracks of the photo-electrons. The number of forward and backward tracks were counted and their ratio determined



Experimental arrangement for photographing photo-electron tracks.

The apparatus was arranged as illustrated in the figure.

A beam of X-rays TC from the molybdenum target of a Coolidge tube driven at 30 k.v. and about 20 m.a. was directed through the lead slits SS and a zirconium phosphate filter F into the expansion chamber C of a Wilson cloud expansion apparatus. The purpose of the slits was to limit the beam and hence afford a control of the number of tracks. Too many tracks destroy the value of a photograph, since one is unable visually to untangle the tracks and clearly distinguish which end is the origin of the track. Zirconium was used as a filter since it is particularly transparent to the K_α line of molybdenum, while highly absorbent of the K_β and K_γ lines and of the white radiation.

On the under side of the plate-glass top of the expansion chamber was a thin film of gelatin made conducting by a small amount of boric acid. On the top of the piston forming the bottom of the chamber was a similar conducting layer of gelatin made black by india ink. A difference of potential of about 60 volts per cm. was maintained across the expansion chamber until just before the expansion.

In taking the photographs a very intense instantaneous illumination is necessary. Some preliminary experiments showed that tungsten filaments exploded by the discharge of a high-tension condenser furnish a satisfactory illumination. A single three mil tungsten filament 10 cm. long placed at the focus of a semicylindrical mirror was found sufficient. The condenser which furnished the current to explode the filament was charged by a small 30 k.v. transformer with thermionic valve in circuit. The light was directed into the expansion chamber through a slit in a black paper covering the top of the chamber. The chamber and camera were, of course, protected by suitable screens.

The photographs were taken with a stereoscopic camera. The matched lenses were marked 5·5 focus f. 4·5. The distance between lenses was 7·3 cm., and they were operated at full aperture. The photographic plate was placed vertical and parallel to the beam. This was considered to be the best position of the plate for examining the forward and backward tracks. Graflex Seed 60 plates were found satisfactory.

The timing of the various events was managed by a heavy pendulum having suitable devices placed in its path. After the room had been darkened and the camera opened the pendulum was released. This caused the following events to occur:—A weight was released which pulled the cork separating the under side of the piston from a vacuum chamber, thus causing the expansion. The electric field across the chamber was removed and the top and bottom gelatin plates were short circuited. (It was found necessary to do this, as otherwise they acted as a condenser and maintained the electric field across the chamber for a sufficient time to affect the shape of the tracks.) The X-rays were started by closing a switch in the primary of the transformer driving the X-ray tube. The tungsten filament was exploded thus illuminating the tracks for the photograph. The timing of these events was adjusted by trial to give a satisfactory picture.

Experimental Results.

About 50 stereoscopic pictures of the tracks of photo-electrons ejected from air by the homogeneous K_a radiation from molybdenum were obtained. The following general observations may be made:—The number of tracks whose initial directions had a forward component greatly exceeds the number of tracks which started with a backward component. About 30 per cent. of the tracks counted started nearly at right angles to the beam of X-rays. Not more than 1 per cent. of the tracks started either exactly forward or exactly backward. Most of the tracks started within 45° of the plane normal to the beam of X-rays.

Three distinct types of tracks could be clearly distinguished: (1) a set of tracks having no appreciable length, (2) a set averaging about ·5 cm. in length, and (3) a set averaging about ·9 cm. in length. The first set is the type C. T. R. Wilson calls sphere tracks. He attributes them to the K radiation of argon ejecting from oxygen or nitrogen, the argon having been put into a state to radiate by having lost one of its K electrons through ejection by the primary radiation. The second set is probably due to the photo-electrons ejected from the argon K ring by the primary X-rays. The third and longest set may be attributed to the photo-electrons ejected from oxygen and nitrogen K rings by the primary X-rays.

A count was made of tracks which started with a forward component along the beam and also a count of those which started with a backward component. In each case only those tracks were counted both of whose ends could be clearly distinguished and where no doubt existed as to which end was the origin of the track. The result of this was that a larger proportion of the short argon tracks were counted, since they are shorter and consequently more easily distinguished among a tangled set of tracks. By count it appears that about 59 per cent. of the tracks counted were due to photo-electrons ejected from the argon K ring, while about 41 per cent. were from oxygen and nitrogen K rings.

These latter could not be distinguished from each other as their difference in length of track was too small. The results obtained by one observer were 188 forward tracks and 69 backward tracks, giving a ratio of 2·74. A second observer found 206 forward and 68 backward tracks, giving a ratio of 3·03. The average ratio of forward to backward tracks is then 2·89.

Discussion.

Rutherford states[15] that the results obtained by previous observers using plates as source of photo-electrons are not inconsistent with the view that all the photo-electrons proceed initially exactly forward with the radiation. The photographs obtained by Wilson[12], by Bubb[13], and those obtained in this experiment show, however, that a large number of the tracks plainly start with a component backward. This seems to decide definitely against Rutherford's view.

Richardson has proposed[16] the view that the radiation pressure in the forward direction is the cause of the excess number of forward photo-electrons. He points out that the momentum of the quantum in the forward direction as given by the electromagnetic theory is $mv = h\nu/c$. We might suppose that this momentum, as well as the energy of the quantum, is given to the photo-electron.

A quantum theory of this effect based on the following hypothesis has been proposed by Bubb[17]: "A quantum of radiant energy which ejects a photo-electron from an atom imparts its energy $h\nu$ to the atom by means of an impulse which has the constant forward component $h\nu/c$ and a sideways component in the direction of the electric vector of the radiation." The orbital electron just previous to its conversion into a photo-electron is assumed to have its momentum in a random direction given in magnitude by the Bohr theory. On this basis the ratio of the forward to the backward photo-electrons is calculated to be

$$R = \{\lambda\sqrt{82{\cdot}44\lambda_0 - 1} + \lambda_0 - {\cdot}0242\}/\{\lambda\sqrt{82{\cdot}44\lambda_0 - 1} - \lambda_0 + {\cdot}0242\},$$

where λ is the wave-length in Å. of the homogeneous radiation causing ejection and λ_0 is the critical ionization wave-length in Å. of the element from which the photo-electron is ejected.

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[15] Rutherford, 'Radioactive Substances and their Radiations,' p. 275.

[16] Richardson, Phil. Mag. xxv. p. 144 (1913).

[17] See present number of Phil. Mag. p. 824.

To apply this formula we have the following data:—The average wave-length of the K_α doublet of molybdenum is $\lambda = \cdot 71$ Å. The critical ionization wave-lengths of the principal constituents of the air are: argon $\lambda_0 = 3\cdot 87$, oxygen $\lambda_0 = 23\cdot 9$, and nitrogen $\lambda_0 = 31\cdot 0$. The formula gives the corresponding values of R as follows: argon $R = 1\cdot 88$, oxygen $R = 7\cdot 32$, and nitrogen $R = 13\cdot 2$. It may be seen that the experimental value 2·89 is larger than the value for argon and less than the values for oxygen and nitrogen and is of the proper order of magnitude.

On the basis of the absorption formula $\lambda^3 Z^4 N$ (where λ is the wave-length of the radiation producing ejection, Z is the atomic number of the source of the photo-electron, and N is the number of atoms present) C. T. R. Wilson has calculated that 15 per cent. of the tracks in air should be from argon, 25 per cent. from oxygen, and 60 per cent. from nitrogen. It is certain, however, by actual observation of length of track, that in the present experiment about 59 per cent. of the tracks counted were from argon, and the remaining 41 per cent. from oxygen and nitrogen. As explained above, this is due to the fact that the short argon track can be more easily untangled visually from a large number or group of interlacing tracks than can the longer tracks from oxygen and nitrogen. On the basis of Wilson's figures the 41 per cent. may be divided into two classes, 13 per cent. from oxygen and 28 per cent. from nitrogen. The composite ratio[18] should then be theoretically,

$$R = (1\cdot 88 \times \cdot 59/2\cdot 88 + 7\cdot 32 \times \cdot 13/8\cdot 32 + 13\cdot 2$$
$$\times \cdot 28/14\cdot 2)/(\cdot 59/2\cdot 88 + \cdot 13/8\cdot 32 + \cdot 28/14\cdot 2) = 3\cdot 38.$$

The experimental ratio 2·89 agrees within 15 per cent. of the theoretical value. In view of the comparatively small number of tracks and the fact that the air is a mixture of so many gases, this agreement is good confirmation of the theory upon which the formula was based.

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[18] It was at first considered possible from an experiment on air to find separate ratios for all three gases, argon, oxygen, and nitrogen. Although it is generally possible to distinguish between an argon track and a track from oxygen or nitrogen, even this cannot always be done, while it is altogether impossible to distinguish between a track from oxygen and one from nitrogen. In view of this a composite or average ratio is given for the mixture rather than the very uncertain separate ratios for the individual gases.

It is proposed to continue these researches by repeating the experiment with only pure gases in the expansion chamber.

I wish to thank Professor F. W. Bubb for advice and assistance in performing this experiment and for criticism of the manuscript.

LXXXVII. *A Quantum Theory on the Asymmetries in the Direction of Ejection of Photo-electrons.* By FRANK W. BUBB, *National Research Fellow, University of Chicago* *.

INTRODUCTION.

TWO types of asymmetry in the direction of ejection of photo-electrons produced by high-frequency radiation have been noted. These two asymmetries may be distinguished by the term "longitudinal" and "lateral."

Longitudinal Asymmetry.—Mackensie[1] first showed that unequal photo-electric currents are obtained from the two sides of a thin plate bombarded normally by gamma rays. A larger current is obtained from that side of the plate from which the gamma rays emerge than from that side upon which the gamma rays are incident. Experiments in which the ratio of the emergent to the incident photo-electric current was measured have been performed by Bragg[2] with gamma rays, by Stuhlmann[3] and Kleeman[4] with ultra-violet light, and by Cooksey[5] and Beatty[6] with homogeneous X-rays. The results of these experiments indicate that the asymmetry increases with the hardness of the radiation, the ratio of emergent to incident current increasing from 1·17 for ultra-violet light upon platinum films to as high as 20 for gamma rays traversing carbon plates.

C. T. R. Wilson[7] and the writer[8] have presented visual evidence of this effect in cloud-expansion photographs of the tracks of photo-electrons. In discussing his photographs, Wilson notes that a majority of the tracks have a forward component comparable with the lateral component. The writer, from an examination of his own photographs, obtains the result that 17 per cent. of the tracks have an initial backwards component, 32 per cent. are ejected almost exactly at right angles to the beam of X-rays, and 51 per cent. have an initial forward component.

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* Communicated by the Author.

[1] Mackensie, Phil. Mag. xiv. p. 176 (1907).

[2] W. H. Bragg, Phil. Mag. xv. p. 663 (1908).

[3] Stuhlmann, Phil. Mag. xxii. p. 854 (1911).

[4] Kleeman, 'Nature,' May 19 (1910).

[5] Cooksey, Phil. Mag. xxix. p. 37 (1912).

[6] Beatty, Proc. Camb. Phil. Soc. xv. 6, p. 492 (1910).

[7] C. T. R. Wilson, Proc. Roy. Soc. civ. (1923).

[8] F. W. Bubb, Phys. Rev. ii. p. 137 (1924).

The work of Beatty [6] and Piersol [9] shows that this effect is due to the excess number of forward over backward photo-electrons, for both these observers find the same velocity for forward and backward photo-electrons. This result is further supported by the photographs of Wilson [7] and by those of the writer [8] which show that the forward and backward tracks have the same average range.

Lateral Asymmetry.—The writer has photographed by Wilson's cloud method the tracks of photo-electrons ejected from air by plane polarized X-rays. These photographs show [8] a strong concentration of photo-electrons ejected nearly parallel to the electric vector of the polarized radiation, and consequently in a single direction perpendicular to the beam. This effect has also been observed by Wilson [7]. As a consequence of this lateral asymmetry, one should expect most of the photo-electrons ejected by unpolarized radiation to be at random in directions nearly normal to the beam. In this case, however, there should be no asymmetry with respect to any particular line normal to the beam as in the case with polarized beams. The effect with unpolarized beams has been previously noted by A. H. Compton [10].

Quantum Impulse Hypothesis.

These two types of asymmetry suggest the following hypothesis, which, it may be shown, is sufficient to account for a number of the photo-electric phenomena. A quantum of radiant energy which ejects a photo-electron from an atom imparts its energy $h\nu$ to the atom by means of an impulse which has the constant forward component $h\nu/c$ and a sideways component in the direction of the electric vector of the radiation.

This hypothesis really consists of three parts. In the first place, it assumes that the whole energy quantum $h\nu$ is given to the atom[11]. This view will, of course, meet with general acceptance; for the work of Millikan[12] on Einstein's photo-electric equation definitely identified the constant with Planck's constant h. The beautiful work of de Broglie[13] with X-rays and of Ellis[14] with gamma-rays, on the magnetic spectrum of photo-electrons, shows that Einstein's equation can be put in the form

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[9] Piersol, Phys. Rev. ii. p. 144 (1924).

[10] A. H. Compton, Bull. Nat. Res. Coun. no. 20, p. 25 (1922).

$$h(\nu-\nu_0)=mc^2(1/\sqrt{1-\beta^2}-1),$$

where ν_0 is the critical ionization frequency (the other quantities have their usual meaning) corresponding to the particular energy level from which the photo-electron is (assumed to be) ejected. In view of this, it is generally accepted that the photo-electron receives initially the whole energy quantum, and that its smaller kinetic energy on emerging is accounted for by the energy loss in escaping from the atom.

In the second place, the hypothesis assumes that the atom receives a forward impulse $h\nu/c$. In support of this view, it may be pointed out that both the classical electromagnetic theory and the relativity theory attribute momentum to energy in motion, and both agree in assigning the momentum $h\nu/c$ to the quantum $h\nu$ in motion with the velocity of light. A. H. Compton's work[15] on the change of wave-length due to the scattering process lends additional support to this view; for Compton treats, in effect at any rate, the quantum as though it were a corpuscle of forward momentum $h\nu/c$, which is scattered simply by bouncing off an electron. Surely on this view then, if the quantum delivers all its energy (itself, so to speak) to the atom, we may reasonably suppose all its forward momentum to be also delivered to the atom. This assumption has been used previously by O. W. Richardson[16] in an attempt to explain the Mackensie asymmetry.

Finally, we assume that a sideways impulse parallel to the electric vector of the radiation also acts on the photo-electron to eject it. The writer's work on the lateral asymmetry in the direction of ejection of photo-electrons produced by polarized X-rays is good experimental support for this view. Furthermore, it is to be expected on the classical electromagnetic theory that the electric force of the radiation is effective in ejecting the photo-electron.

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[11] The term atom will be used to denote the system before ejection of the photo-electron. The portion of the atom which remains after ejection of the photo-electron will be called the photo-atom. In this sense, then, the atom consists of two parts—the photo-electron and the photo-atom.

[12] Millikan, Phys. Rev. vii. p. 355 (1916).

[13] M. de Broglie, *Jour. de Phys. et Rad.* ii. p. 265 (1921).

[14] Ellis, Proc. Roy. Soc. xcix. p. 261 (1921).

[15] A. H. Compton, Phys. Rev. xxi. p. 284 (1923).

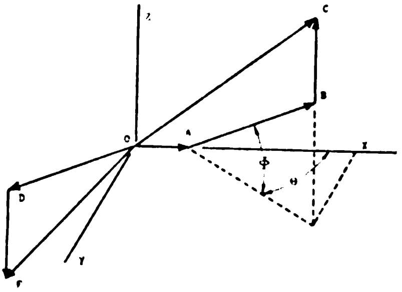
[16] Richardson, 'The Electron Theory of Matter,' p. 478.

This hypothesis has the virtue of supplying us with a momentum relation in addition to the Einstein photo-electric relation. We cannot expect the Einstein equation, concerned only with energy, to supply a complete dynamical basis for the explanation of the photo-electric effect.

Momentum and Energy Relations.

The principle of the conservation of momentum requires that the vector sum of the momentum of the system, which we shall suppose to consist only of the quantum, the photo-electron, and the photo-atom[11], shall be the same before and after separation.

Fig. 1.



The momentum relations involved in the ejection of a single photo-electron by a single quantum of radiation.

In fig. 1 let O be the position of an atom about to be disrupted by a quantum $h\nu$ proceeding in the direction OX and having its electric vector parallel to OZ (the radiation is then in the usual sense polarized in the XY plane). Before ejection of the photo-electron the momentum consists of three parts: the momentum

$$h\nu/c = \mathrm{OA}$$

of the quantum; the momentum

$$m\beta_0 c/\sqrt{1-\beta_0^2} = \mathrm{AB}$$

of the photo-electron in its atomic orbit, where m is its rest mass and β_0 the ratio of its velocity to c, the velocity of light; and the momentum OD of the photo-atom. If we assume that the momentum of the whole atom is negligible, the momentum OD of the photo-atom before separation is equal and opposite to that of the orbit-electron. After separation the momentum consists of two parts: the momentum

$$m\beta c/\sqrt{1-\beta^2}=OC$$

of the photo-electron, where β is the ratio of its velocity to that of light; and OF, the final momentum of the photo-atom.

According to our hypothesis, an impulse (represented by BC in fig. 1) acts upon the photo-electron to eject it. Hence the final momentum OC of the photo-electron may be thought of as consisting of three parts: OA, AB, and BC[17]. Accordingly we write the vector equation

$$OA+AB+BC=OC. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If we assume that the photo-atom acts as the seat of the reaction to the impulse BC, the final and initial momenta of the photo-atom differ vectorially by $DF=-BC$. This assumption is by no means necessary; for we might assume that the reaction to the impulse BC has its seat upon the source of the radiation, or upon the æther, or upon another electron[18], or we might even assume (as Lorentz has done under quite similar circumstances) that no reaction exists. Equation 1 is true, no matter which one of these views we may favour.

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[17] It is true that on the Bohr theory of the atom there is a binding force of electrostatic attraction between the nucleus and electron. The principal effect of this force is to abstract a certain amount of kinetic energy from the photo-electron by virtue of the distance through which the electron moves in escaping. But the time of escape is also a factor, for the more slowly the photo-electron escapes, the greater is the effect of the binding force in changing its direction of ejection. This is analogous to the effect of the speed of β-particles on their scattering by matter. The β-particles are supposed to travel in hyperbolæ, and to leave the centre of attraction with the same kinetic energy as that which they had before close approach. The entire effect of the attraction of the scattering nucleus (unless capture occurs) is to deflect the β-particle—the slower the β-particle the greater its deflexion. So far, comparison of our results with experiment does not oblige us to take account of the time of escape of the photo-electron in permitting the binding force to modify the direction of ejection of the photo-electron.

[18] Some photographs published recently (Proc. Roy. Soc. fig. 22, plate 12, civ. 1923) by C. T. R. Wilson may be interpreted as evidence for this view. These photographs show strange pairs of associated photo-electron tracks, both starting near the same point in the beam of X-rays and having about the same range. Now, if the photo-electron is ejected by a sideways impulse, it seems natural to look for evidence of an equal and opposite reaction impulse. We might suppose the quantum to exert a sideways impulse upon one electron, and its equal and opposite reaction impulse upon another electron, and consequently divide its energy about equally between the two. In this way we should get such pairs as Wilson finds. Wilson states that there is a great tendency for the line joining the points of origins of the two members of a pair to be nearly perpendicular to the primary X-ray beam. This observation is in accord with the present view. If the nucleus serves as the seat for the reaction impulse, it should receive, due to its great comparative mass, but a small part of the energy quantum. In this case we should get only one photo-electron—the ordinary case.

The principle of the conservation of energy requires that the energy of the system be the same before and after separation. Before separation the energy of the system consists of the quantum and the energy in the atom. After separation the energy consists of the kinetic energies of the photo-electron and photo-atom and the energy of the separated system. Accordingly, if w be the energy required to separate the photo-electron and photo-atom, and E the kinetic energy of the photo-atom[19], we have

$$h\nu = \mathrm{E} + mc^2(1/\sqrt{1-\beta^2}-1) + w. \quad . \quad . \quad . \quad (2)$$

We might write next the vector momentum equation OD − BC = OF for the photo-atom, and then eliminate BC from this equation and Eq. 1. The resulting equation could then be solved with Eq. 2 for the momenta of the photo-electron and photo-atom. However, this leads to rather complicated expressions, which may be avoided by dropping the negligible term E from Eq. 2. This term is negligible because the mass of the photo-atom is of the order 2000 times that of the photo-electron, and consequently its initial kinetic energy and change in kinetic energy are ordinarily of the order 1/2000 of the kinetic energy of the photo-electron. Dropping the term E from Eq. 2 gives

$$h\nu = mc^2(1/\sqrt{1-\beta^2}-1) + w, \quad . \quad . \quad . \quad . \quad (3)$$

which is the familiar Einstein photo-electric equation. It should be noted that although the kinetic energy of the photo-atom may be negligible in comparison with the kinetic energy of the photo-electron, the momentum change in the photo-atom is by no means negligible.

Statistical Considerations.

Since most experiments on the photo-electric effect are statistical in nature, we shall next consider the relations (1) and (3) as applied to such problems. In order to simplify the treatment, we shall make the following assumptions:—(*a*) The radiation ejecting the photo-electron is homogeneous. This requires ν to be constant. (*b*) The momentum vector of the electron in its atomic orbit is at random—that is, AB is random. (*c*) The momentum vector AB is constant in magnitude. This requires that all the photo-electrons be ejected from the circular K rings of the atoms. (*d*) The term w in Eq. 3 is constant in magnitude. This will be true if the condition (*c*) be satisfied, for then all photo-electrons will come from the same energy level.

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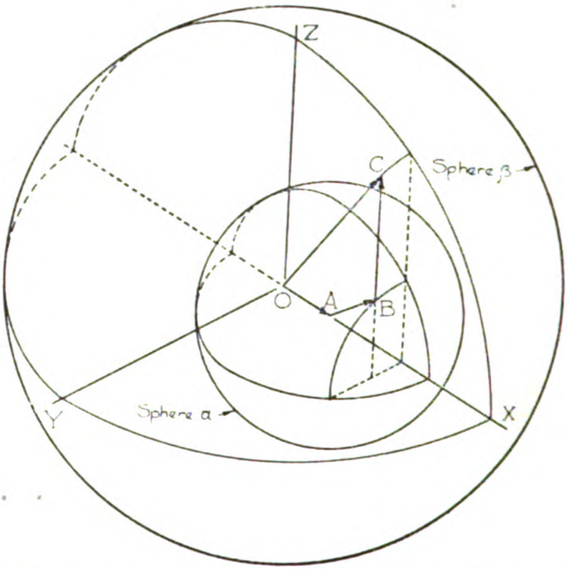
[19] Assuming that the reaction actually acts upon the photo-atom as the most likely hypothesis.

In the light of these restrictions let us reconsider fig. 1 and develop from it fig. 2. Since the initial momentum vector AB of the photo-electron is constant in magnitude and random in direction, the vector AB (see fig. 2) ends on a sphere (which we shall call α) of fixed centre A and radius

Fig. 2



Graphical representation of the momentum relations involved in the ejection of a large number of photo-electrons. This contains within its geometry many consequences of the present theory.

$$AB = m\beta_0 c / \sqrt{1-\beta_0^2}.$$

From the restrictions (*a*) and (*d*) and Eq. 3 it is easy to see that the final momentum vector

$$OC = m\beta c / \sqrt{1-\beta^2}$$

is constant in magnitude, and hence ends on a sphere (which we shall call β) of fixed centre O and radius

$$OC = \sqrt{(mc^2 + h\nu - w) - m^2c^4} / c.$$

Although the point B is at random on sphere α, the point C is not at random on sphere β; for by hypothesis the impulse BC is parallel to OZ. Hence point C is to be located by finding the point of intersection of sphere β with a line drawn through B parallel to OZ.

These various relations are exhibited in fig. 2, which contains within its geometry many of the immediately useful results of the present theory.

Applications of the Theory to Experiments.

Longitudinal Asymmetry.—In fig. 2 let the YZ plane represent a thin plate or film of matter traversed by unpolarized radiation proceeding in the direction OX. The photo-electrons which are ejected from the plate may be divided into two classes: those leaving the plate on the forward or emergent side (positive side of YZ plane), and those leaving the plate on the backward or incident side. It is the ratio of the forward to the backward photo-electric current which Bragg, Cooksey, and Beatty measured in their experiments mentioned above. We proceed to calculate this ratio in view of the present theory.

From fig. 2 it is clear that all the photo-electrons of the forward class have their final momentum vectors OC ending on that portion of sphere β to the right of the YZ plane, and their initial momentum vectors AB ending on that portion of sphere α to the right of the YZ plane. Similarly, all photo-electrons of the backward class have their final and initial momentum vectors ending respectively on those zones of spheres β and α to the left of the YZ plane. If we suppose that we are dealing with a sufficiently great number of photo-electrons to justify a statistical treatment, we can say that the ratio R of forward to backward photo-electric current is equal to the ratio of the area of the zone of of sphere α on the right of the YZ plane to the area of the zone of sphere α on the left of the YZ plane. But these areas are in the ratio of their altitudes, from which we get the equation

$$\mathrm{R} = (\mathrm{AB}+\mathrm{OA})/(\mathrm{AB}-\mathrm{OA}). \quad . \quad . \quad . \quad (4)$$

The initial momentum AB of the electron in its atomic orbit may be expressed in terms of its energy of binding $h\nu_0$ by the formula [20]

$$\mathrm{AB} = m\beta_0 c / \sqrt{1-\beta_0^2} = mc\sqrt{2\alpha_0-\alpha_0^2}/(1-\alpha_0), \qquad (5)$$

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[20] Calculated on the basis of the Bohr theory of the atom for circular orbits only, such as the K rings. For circular orbits the momentum of the electron in its atomic orbit is constant as demanded by our restriction (*c*). For elliptical orbits our momentum vector AB would not be constant in magnitude.

where $\alpha_0 = h\nu_0/mc^2$. Remembering that $OA = h\nu/c$ and letting $\alpha = h\nu/mc^2$ and substituting Eq. 5 in Eq. 4, we get

$$R = \{\sqrt{2\alpha_0 - \alpha_0^2} + \alpha(1-\alpha_0)\} / \{\sqrt{2\alpha_0 - \alpha_0^2} - \alpha(1-\alpha_0)\}. \quad (6)$$

Putting in the numerical values of h, m, and c and expressing λ and λ_0 in Angström units, we have, finally,

$$R = \{\lambda\sqrt{82 \cdot 44\lambda_0 - 1} + \lambda_0 - 0 \cdot 0242\} / \{\lambda\sqrt{82 \cdot 44\lambda_0 - 1} - \lambda_0 + 0 \cdot 0242\}, \quad (7)$$

where λ is the wave-length in Å. of the radiation ejecting the photo-electrons, and λ_0 is the critical ionization wave-length in Å. of the atom from which the photo-electrons are ejected. A fairly complete list of the critical ionization wave-lengths for various atoms has been tabulated by Duane[21].

The Eq. 7 is subject to the condition that the quantum $h\nu$ possess sufficient energy to eject the photo-electron—that is, we must have

$$\lambda < \lambda_0. \quad \ldots \ldots \quad (8)$$

In Bragg's experiments[2] on this longitudinal asymmetry, the source of the radiation (gamma rays) was held constant (λ constant) while the source of the photo-electrons was varied (λ_0 varies). The ratios as determined experimentally by Bragg for various substances are considerably smaller than the corresponding theoretical ratios as calculated from Eq. 7. However, this is to be expected since Bragg used very thick plates. In the first place, photo-electrons ejected from layers inside a thick plate must suffer many deflexions in passing out. It is not difficult to see that this tends to cut down the forward and increase the backward photo-electrons. Again, thick plates absorb the radiation as well as the photo-electrons, so that if the plate were sufficiently thick we should get nothing out of it except incident photo-electrons. Indeed, Rutherford[22], in considering the effect of scattering of the photo-electrons by thick plates, regards Bragg's results as conflicting in no way with the assumption that all the photo-electrons are ejected initially in the direction of the radiation. A comparison of theoretical with these experimental ratios brings out the essential agreement that both increase as the atomic number of the source of the photo-electrons decreases.

In Beatty's experiments[6] the source of the photo-electrons was held constant and the wave-lengths of his homogeneous X-rays were varied. A comparison brings out the additional essential agreement that R increases as the hardness of the radiation increases. In these results the theoretical ratio again exceeds the experimental. The reason is again probably because the plates were too thick. Beatty's source of photo-electrons was a film of silver estimated to be 1100 atoms thick.

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[21] Duane, Bull. Nat. Res. Coun. no. 6 (1920).

[22] Rutherford, 'Radioactive Substances and their Radiation,' p. 275.

Cooksey's results[5], shown in Table I., may be expected to furnish a more rigorous test of the present theory. Cooksey determined the ratios for various thicknesses of plate, and extrapolated to find the ratio corresponding to zero thickness. These extrapolated ratios are given together with the corresponding theoretical ratios in Table I. These results are seen to be in good agreement numerically.

Table I.

Source of Radiation.	Source of Photo-electrons.			
	Gold.		Silver.	
	R exp.	R cal.	R exp.	R cal.
Chromium	1·20	1·23	1·24	1·20
Iron	1·24	1·28	1·21	1·24
Zinc	1·21	1·21	1·20	1·34
Tin	1·16	1·51	1·23	1·37

In some recent experiments by O. K. de Foe[23] this ratio was measured by counting the forward and backward tracks produced inside a Wilson cloud expansion apparatus by the homogeneous K_α radiation from molybdenum. The experimental ratio thus found was 2·89, while the theoretical ratio according to Eq. 7 is 3·38. These values agree within 15 per cent., which seems to be good evidence for the present theory.

Lateral Asymmetry.—Suppose a photographic plate to be erected parallel to the YZ plane of fig. 1—that is, normal to the direction OX of the radiation ejecting the photo-electrons. We wish to calculate the distribution, as regards initial direction of ejection of the photo-electrons ejected by polarized radiation, appearing on a Wilson cloud photograph on such a plate. The writer has performed an experiment[8] with the apparatus thus briefly outlined in which the radiation along the OX axis was plane polarized with the electric vector parallel to the OZ axis. A strong concentration of photo-electrons ejected nearly parallel to the electric vector was discovered.

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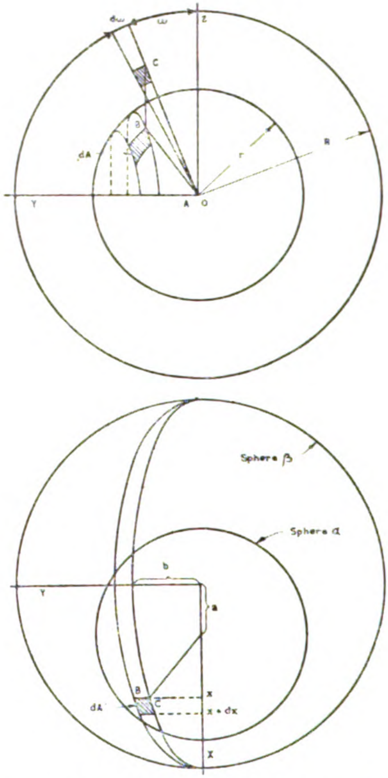
[23] See present issue of the Phil. Mag. p. 817.

Fig. 3.



The momentum relations involved in the ejection of a large number of photo-electrons by polarized radiation.

Pass two planes through the line OX making the angle $d\omega$ with each other and the angle ω with the XZ plane. These two planes cut the sphere β in two great circles which bound a lune on the surface of sphere β. Let us represent the projections of spheres α and β upon the XY and YZ planes, somewhat as the engineer shows a plan and elevation (see fig. 3). The projection of the lune defined above is shown on the XY plane as bounded by two ellipses, and its projection upon the YZ plane as two radii.

All photo-electrons whose final momentum vectors OC end on the lune have their initial momentum vectors AB ending on a small area of sphere α, which is bounded by two skew curves. These two skew curves are the projections on α of the two great circles on β, and are defined by projectors all of which lie on the surface of an elliptical cylinder whose elements are parallel to the OZ axis. These curves are hidden by the ellipses in the plan, but appear separately in the elevation.

Since a sufficiently large number of tracks will give a uniform distribution of initial momentum vectors AB over the surface of α, it is clear that the relative number of tracks on the photographs whose initial portions lie within the angle $d\omega$ to the total number of tracks is equal to the ratio of one of these elementary areas on α to the whole area of α. The two projecting cylinders cut two elementary areas out of α, one on the upper and one on the lower hemisphere. Since each of these may be supposed to contribute only one-half its photo-electrons to the lune (the other halves going to a symmetrical lune on the lower hemisphere of β), the element to be used in the above ratio may be taken as that on one hemisphere of α.

It therefore becomes necessary to calculate one of these elementary areas of α. Pass two planes perpendicular to the OX axis, one at x and the other at $x+dx$. Each plane cuts a circle from α. These two circles cross both skew curves on α, and thereby bound a small area which we shall call dA. The projection of dA upon the XY plane is bounded by two infinitesimal straight lines and two infinitesimal elliptical arcs. We shall call this projected area dA'. We have at once

$$dA' = dx\,dy,$$

where y is given by the ellipse

$$y = \sqrt{R^2 - x^2}\sin\omega.$$

Accordingly we have

$$dA' = \sqrt{R^2 - x^2}\cos\omega\,d\omega\,dx.$$

Supposing dA to be so small that second-order terms may be neglected, the angle between the "plane" dA and its projection dA' has for its cosine the value z/r. Hence we have

$$dA = r\sqrt{R^2 - x^2}\cos\omega\,d\omega\,dx\,/\,z,$$

in which, besides the variable x, there appears nothing but z. The variable z may be expressed in terms of x by eliminating y between the equation of the ellipse given above and the sphere

$$z^2+y^2+(x-a)^2=r^2.$$

Hence we have finally

$$dA=r\sqrt{R^2-x^2}\,d\omega\,dx\,/\sqrt{A^2-(x-B)^2},$$

where
$$A^2=\sec^2\omega(r^2+a^2\tan^2\omega-R^2\sin^2\omega)$$

and
$$B=a\sec^2\omega.$$

The limits between which dA is to be summed are x_1 and x_2, the two roots of x found by solving simultaneously the ellipse and circle given by the respective equations

$$y=\sqrt{R^2-x^2}\sin\omega \quad\text{and}\quad y^2+(x-a)^2=r^2.$$

This gives
$$x_1=B-A \quad\text{and}\quad x_2=B+A.$$

Since the number of tracks per unit area is $N/4\pi r^2$, we have finally

$$dN/d\omega=N/4\pi r\int_{B-A}^{B+A}\sqrt{R^2-x^2}\,dx/\sqrt{A^2-(x-B)^2}. \quad (9)$$

After some reduction this expression becomes

$$\begin{aligned}dN/d\omega&\\ =N/4\pi r\{&F(\pi/2,k)(R-A-B)\sqrt{(R+A-B)/(R+A+B)}\\ &+E(\pi/2,k)\sqrt{(R+A-B)(R+A+B)}\\ &+\Pi(\pi/2,n,k)2B(R-A-B)\,/\,\sqrt{(R+A)^2-B^2}\}, \quad (10)\end{aligned}$$

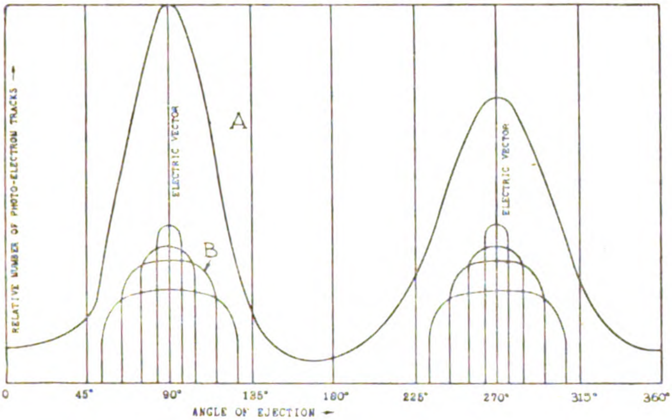
where $F(\pi/2,k)$, $E(\pi/2,k)$, and $\Pi(\pi/2,n,k)$ are the complete elliptical integrals of the first, second, and third kinds respectively. The modulus

$$k=2\sqrt{AR/[(R+A)^2-B^2]},$$

and the parameter
$$n=-2A/(R+A-B).$$

Fig. 4 furnishes a comparison between an experimental curve[8] and several curves calculated from theory. Curve A shows the relative number of photo-electrons ejected at all angles by heterogeneous polarized X-rays. The source of the X-rays was a Coolidge tube with a tungsten target operated at about 50,000 volts by a transformer. The X-rays were polarized by scattering from a paraffin block at 90°. Curves B were calculated from Eq. 9 by graphical integration. Each of the curves B represents the theoretical distribution for a homogeneous radiation ejecting electrons from the nitrogen K ring. The width of a particular curve depends on the hardness of the radiation—the harder the radiation, the narrower the hump. The height of a particular hump depends on the intensity of the corresponding radiation. Several of these curves are shown for the purpose of bringing out the possibility that the curve A is the sum of a number of such curves B corresponding to the various lengths of X-rays making up the heterogeneous beam used in obtaining the curve A. The Eq. 9 requires that the radiation producing the ejection be homogeneous, and also that all photo-electrons come from the same energy level. In order, then, to calculate a curve to compare with curve A, it is necessary to know the wave-length and intensity of all the radiation as well as the relative number of photo-electrons

Fig. 4.



Comparison of experimental and theoretical curves, showing the distribution of photo-electrons ejected by plane polarized radiation.

ejected from the various gases—nitrogen, oxygen, argon, etc.—which were present in the expansion chamber. The comparison presented in fig. 4 is then only for the purpose of showing qualitative agreement. Experiments are in progress in which it is hoped to settle the question of quantitative agreement.

Discussion.

The present theory admits of a number of tests, only three of which have been considered here. The experiments of Bragg and Beatty on the Mackensie asymmetry give qualitative support to the theory, in that the theoretical ratio of forward to backward photo-electric current varies both with hardness of the radiation and with source of the photo-electrons in the same way as the experimental ratio varies The experiments of Cooksey and of de Foe on the same asymmetry are in close numerical agreement with the predictions of the theory. The writer's experiments with polarized X-rays, in which the tendency for the photo-electrons to proceed in the direction of the electric vector was discovered, also support the theory qualitatively. The theory further agrees with the results of Beatty and Piersol, in that it predicts the velocity of ejection to be independent of the direction of ejection.

A number of additional predictions of the theory have been omitted from the present paper, since experimental work in progress for the purpose of testing them has not been carried far enough. In particular, we mention that the theory offers certain information on the time of action between the quantum and electron when the binding force between the electron and nucleus is taken account of.

Apart from the well-known difficulties which the wave theory has in explaining the Einstein photo-electric relation, the present theory introduces nothing contradictory to the wave theory. If we favour the corpuscular viewpoint, however, it appears that the orthodox view of the quantum as a scalar bundle of energy must be modified to account for the lateral asymmetry in the direction of ejection of photo-electrons. We may view the quantum as a "vector quantum," since it appears to exert a sideways impulse to eject the photo-electron.

LXXXVIII. *On the Universal Distance of the Order of 10^{-8} cm. between the Centres of Nearest Atoms.* By ALBERT C. CREHORE *.

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I. *Introductory.*

THIS title has been chosen to emphasize a well-known experimental result of crystal analysis, which is seldom stressed, but which is of the utmost importance and is the key to the proper understanding of the structure and behaviour of atoms. The distance between centres of the nearest adjacent atoms in crystals is in round numbers found experimentally to be of the order of 10^{-8} cm. rather than 10^{-7}, 10^{-9}, or 10^{-10} cm. It may be as small as $\cdot 5 \times 10^{-8}$ cm. or as large as 4×10^{-8} cm. in special cases perhaps, but the minimum distance always falls within these rather narrow limits. Considering the very small size of the electron itself, which is now experimentally established, the experimental and theoretical dimensions agreeing very satisfactorily, and taking into account that this negative electron is the largest fundamental body of charge that enters into the structure of an atom, for the negative electron occupies a far greater volume than any positive charge: taking these things into consideration, it is not at all evident why 10^{-8} cm. instead of 10^{-7} or 10^{-9} cm. should have been this universal distance. There appears to be plenty of room for distances much smaller or greater than 10^{-8} cm., and it has not been evident why there should exist such a universal distance of any value whatever.

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* Communicated by the Author.

But it is evident from the same facts that there must exist a very definite causal connexion between the constitution or structure of the atoms themselves and this universal distance, for with so many different kinds of atoms one might expect a much wider departure from 10^{-8} cm. than is found experimentally, if there exists no controlling principle within each atom. If, however, it can be shown that this universal distance is closely related to the properties of the atom and negative electron itself and controlled by them, as is shown in this paper, it is not surprising but very natural to expect a universal distance between atomic centres, because the electron forms an integral part of each and every one of these atoms. The main distance itself between the atoms will then be determined by the negative electron, and the very small variations from this main distance will depend upon the particular grouping of these electrons within each atom in the different kinds of atoms.

This subject has been treated in a preliminary way in former papers * from the standpoint of a new atomic model based upon electrodynamics, in which there are no electronic orbits in the steady state of atoms. It is not intended to open this question again here as to whether or not there exist any such steady orbits, but rather to give an account of progress in the mathematical investigation of the new atomic model, with particular reference to this universal distance, above mentioned, of the order of 10^{-8} cm.

Without departing at the outset from the doctrine of electromagnetic theory, no such orbits of negative electrons are admissible in atoms in their steady states, but it is not intended to abandon electrodynamics at any point. Moreover, such a course is not at all necessary. These orbits are not needed. On the other hand, those who have become accustomed to think in terms of orbits may easily attribute

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* A. C. Crehore, Phil. Mag. p. 569, Oct. 1921; p. 886, May 1922; p. 1025, June 1922; p. 33, Jan. 1923.

the universal distance of 10^{-8} cm. to the dimensions of the orbits themselves, which have been computed by means of this same electrodynamics that was abandoned in the matter of radiation of energy from electrons describing orbits. When one pictures a crystal model based upon the stationary-orbit-form of atom, where the revolving electrons come very close together at certain points and depart far asunder again at other points, and realizes that it is necessary to postulate no mutual reaction between these orbital electrons such as electromagnetic theory demands, it seems that the time has arrived to search for a more satisfactory form of atomic model, one that does not abandon electrodynamics at the outset.

Quite apart from all thoughts as to the actuality of things, the mathematical aspects of the problem suggested by the new atomic model, with which we are concerned, have many features of great beauty and sufficient merit to maintain the interest, to say nothing of the new field that has been opened for atomic physics. How to give readers an understanding of the subject with the minimum of effort on their part has received some study. The historical order of development would be the easiest, but an objection is that the results become clouded with a mass of detail. It has been necessary, however, to pass through many successive steps to attain the final result to be described, and if these steps were omitted there is a question whether the presentation would have much meaning or be understood.

Let us begin by restating some of the properties of the fundamental bodies, the negative electron and the positive charge of the hydrogen atom, with which the atom and then the molecule of hydrogen are built, as before given in the first paper *. The negative electron in its free state when not forming a part of an atom is supposed to be an oblate spheroid of negative charge $(-e)$ in rotation about its minor axis. The charge is supposed distributed uniformly throughout the volume, which is the equivalent of a sphere of radius

$$r=2\cdot244\times10^{-13}\text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The semi-axes of the meridian section are

$$\left.\begin{aligned} a&=3\cdot257\times10^{-13}\text{ cm.,}\\ b&=1\cdot065\times10^{-13}\text{ cm.,}\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the eccentricity

$$\epsilon=0\cdot945. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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* *Loc. cit.* Phil. Mag. October 1921, p. 589.

The total energy content of the negative electron is equivalent to its mass times the square of the velocity of light. Denoting its mass at zero translational velocity by m_0 and the velocity of light by c, it becomes

$$E_0 = 0{\cdot}898 \times 10^{-27}\, c^2 = 8{\cdot}08 \times 10^{-7} \text{ erg.} \quad . \quad . \quad (4)$$

The positive charge of the hydrogen atom is supposed to be an oblate spheroid with uniformly distributed charge having the same eccentricity as the negative electron, (3) above. But its charge is $+2e$ instead of $-e$ and its dimensions are equivalent in volume to a sphere of radius

$$r = 4{\cdot}86 \times 10^{-16} \text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The semi-axes are

$$\left.\begin{aligned} a &= 7{\cdot}054 \times 10^{-16} \text{ cm.,} \\ b &= 2{\cdot}307 \times 10^{-16} \text{ cm.} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (6)$$

The total energy content of this positive charge is also given by the product of its mass by the square of the velocity of light, namely

$$E = 1{\cdot}66 \times 10^{-24}\, c^2 = 1{\cdot}49 \times 10^{-3} \text{ erg.} \quad . \quad . \quad (7)$$

For comparison it is important to bear in mind that the energy required to separate the two atoms of hydrogen forming one molecule to a great distance from each other is

$$E = 5{\cdot}8 \times 10^{-24} \text{ erg.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

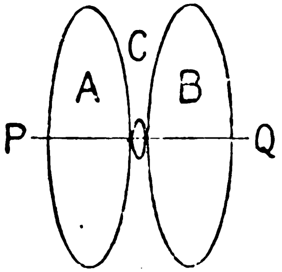
This value has been determined experimentally due to Langmuir, and the order of magnitude of most of the energies of the heats of formation and heats of dissociation in many chemical reactions is well represented by this figure.

The energy content of the negative electron is more than 100,000 times this value, and of the positive charge more than 250,000,000 times it. These facts have a very important bearing upon the whole behaviour of atoms. It seems best to give at the outset the reasoning that shows the important part played by the very large energy content of the electron in the formation of atoms and of molecules. The oblate spheroid given by (2) is supposed to be that of a free electron which is in stable dynamic equilibrium. Two such electrons will be attracted by the positive charge ($2e$) of a hydrogen atom at all distances, and will approach it until they come into contact with it, the three bodies aligning themselves on a common axis as in fig. 1, which represents a meridian section of a hydrogen atom *.

* *Loc. cit.* p. 588.

The pressure of each electron upon the positive charge due to the resultant attraction of the other two bodies must cause a slight flattening of the original figure of the free electron. But to either flatten or to expand the figure of the free electron, which is in dynamic equilibrium, requires that work be done, and, if the amount of this change of shape were known, the energy may be computed, or *vice versa*, if the work done were known, the change in shape may be computed. Now the energy so involved represents the difference between the energies of the free bodies and these same bodies as they exist in the atom, that is to say, it is the energy of ionization of the free hydrogen atom.

Fig. 1.



Meridian section of the hydrogen atom described in the first paper.

But there are two energies of ionization for an atom which carries two electrons—the first when only one electron is detached, and the second when both are detached. The first of these is the only one that has ever been measured for hydrogen, and this will be of little service to us. The second energy must be far greater than the one which has been measured. In fact, it figures so great that the last electron never leaves the positive charge, at least in laboratory experiments so far conducted, and so it cannot of course be measured. And so we have never heard of a hydrogen ion with two positive charges. The maximum it has been possible to give it in the laboratory is one positive charge.

It seems profitable to picture the change that takes place in the atom during the removal of one electron. Were it not for the fact that much of the energy of the electron on the opposite side is transferred over to the one electron during the process of removal of the one, it would not be possible to remove even one, for in the symmetrical position in the free atom of course each electron shares alike and represents one-half of the very large energy of the double ionization. But, when one begins to move away from the centre of the atom, its minor axis expands because of the release of the pressure, and thereby it gives up some of the energy that was expended upon it during the formation of the atom. At the same time the minor axis of the opposite electron must contract slightly because of the increased pressure on that side due to the removal of the first electron, and thus it is apparent that there is a transfer of some of the energy across from the one to the other electron.

The comparatively small difference between the gain of energy of the one that remains and the loss of energy of the one that departs represents the rather small energy of the first ionization of the hydrogen atom. This is known experimentally, but is not of much importance for this problem. The more important energy, which is not known experimentally and probably will not be measured for some time to come, is the second or total ionization energy.

It seems important, however, to attack the problem from the standpoint of energy; and we shall now consider the problem of finding a relation between the energy absorbed or emitted by a negative electron because of a definite change in its semi-minor axis. When the hydrogen atom is formed as in fig. 1 because each electron is attracted at all distances until they both come into actual contact with the positive charge, then the attraction, which still continues, results in a deformation of the shape of the electron. It may be assumed, since this change is extremely small for a comparatively large energy change, that each remains an oblate spheroid as before. The result of the pressure between the electron and the positive charge is to flatten the spheroid slightly, thus increasing its eccentricity and decreasing its semi-minor axis.

II. *The Change in the Energy Content of the Electron for a Given Change in the Semi-minor Axis.*

It will be assumed as before that the volume of the spheroid, which has a uniform distribution of charge throughout, remains constant and fixed, equal to that of a sphere of radius r, given by (1) above. This volume is

$$V = \tfrac{4}{3}\pi r^3. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The volume of an oblate spheroid of polar semi-axis b and equatorial radius a_0 is

$$V = \tfrac{4}{3}\pi a_0{}^2 b. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Equating these volumes gives an immediate relation between a_0 and b:

$$a_0^2 b = r^3 \quad \text{or} \quad \frac{b^2}{a_0^2} = \frac{b^3}{r^3}. \quad . \quad . \quad . \quad . \qquad (11)$$

But in an ellipse the relation between the axes and the eccentricity is

$$\frac{b^2}{a_0^2} = 1-\epsilon^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

Whence, equating (11) and (12), we have

$$\frac{b^3}{r^3} = 1-\epsilon^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

The area of an oblate spheroid S in terms of its semi-axes and eccentricity is

$$S = 2\pi a_0^2 + \frac{\pi b^2}{\epsilon} \log \frac{1+\epsilon}{1-\epsilon}. \quad . \quad . \quad . \quad . \qquad (14)$$

By means of the above relations this area is expressible in terms of the eccentricity alone, as

$$S = 2\pi r^2 \left[(1-\epsilon^2)^{-1/3} + \frac{1}{2\epsilon}(1-\epsilon^2)^{2/3} \log \frac{1+\epsilon}{1-\epsilon}\right]. \qquad (15)$$

From this we wish to find the change in the area of the spheroid that corresponds to a given change in the minor axis; and since this change is extremely small, the differential of S may be used. Differentiating (15) with respect to ϵ gives

$$\frac{dS}{d\epsilon} = 2\pi r^2 \left\{ \frac{2}{3}(1-\epsilon^2)^{-4/3} + \frac{1}{\epsilon}(1-\epsilon^2)^{-1/3} - \left[\frac{2}{3}(1-\epsilon^2)^{-1/3} + \frac{1}{2\epsilon^2}(1-\epsilon^2)^{2/3}\right] \log \frac{1+\epsilon}{1-\epsilon} \right\}, \qquad (16)$$

which in terms of r, b, and ϵ is equivalent to

$$\frac{dS}{d\epsilon} = 2\pi r^2 \left\{ \frac{2}{3}\left(\frac{r}{b}\right)^4 + \frac{1}{\epsilon}\left(\frac{r}{b}\right) - \left[\frac{2}{3}\left(\frac{r}{b}\right) + \frac{1}{2\epsilon^2}\left(\frac{b}{r}\right)^2\right] \log \frac{1+\epsilon}{1-\epsilon} \right\}, \quad . \quad . \quad . \qquad (17)$$

By means of (13) the rate of change of ϵ with respect to b may be obtained by differentiation as follows:

$$\frac{d\epsilon}{db} = -\frac{3}{2\epsilon r}(1-\epsilon^2)^{2/3} = -\frac{3b^2}{2r^3\epsilon}. \quad . \quad . \quad . \qquad (18)$$

The rate of change of the area of the spheroid S with respect to the semi-minor axis b is then the product of (17) by (18). Denoting the brace in equation (17) by $f(b)$ for brevity, we obtain

$$\frac{dS}{db}=\frac{dS}{d\epsilon}\cdot\frac{d\epsilon}{db}=-\frac{3\pi b^2}{r\epsilon}f(b). \quad . \quad . \quad . \quad . \quad (19)$$

When the change in area is small, we may say that dS becomes $\Delta S=S_2-S$, and db becomes $\Delta b=b_2-b$; whence

$$S_2-S=-\frac{3\pi b^2}{r\epsilon}(b_2-b)f(b). \quad . \quad . \quad . \quad . \quad . \quad (20)$$

In accord with the properties of the electron as given in the first paper (see equation (73)), there is a surface tension over the entire surface of the electron given by

$$T=\frac{3}{16}\frac{e^2}{\pi r^2 k}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

To increase its surface by the amount S_2-S and to flatten the electron, thus reducing its minor axis, requires an amount of energy

$$\Delta E=T.\Delta S=T(S_2-S). \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Hence by (20) and (21)

$$\Delta E=-\frac{9}{16}\frac{b^2e^2}{r^3\epsilon k}(b_2-b)f(b). \quad . \quad . \quad . \quad (23)$$

Taking b in round numbers as 10^{-13} cm., and r as given by (1), the eccentricity obtained from (13) is

$$\epsilon=0\cdot 9547. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

So by (23) we find numerically that

$$\Delta E=-\frac{e^2}{k}(\cdot 307\times 10^{26})(b_2-b). \quad . \quad . \quad . \quad (25)$$

Using as the value of the charge, $e=4\cdot 763\times 10^{-10}$ E.S.U., the energy in (25) becomes

$$\Delta E=-6\cdot 964\times 10^{6}(b_2-b), \quad . \quad . \quad . \quad . \quad . \quad (26)$$

which is the expression that was to be found.

III. *The Energy of Double Ionization of the Hydrogen Atom.*

In the free state of the electron the value of b given by (2) above is $1\cdot 065\times 10^{-13}$ cm. If this is contracted down to exactly 10^{-13} when the hydrogen atom is formed, it would mean that

$$b_2-b=(1-1\cdot 065)\times 10^{-13}=-0\cdot 065\times 10^{-13}\text{ cm.} \quad (27)$$

The corresponding energy change by (26) becomes

$$\Delta E = 0{\cdot}4527 \times 10^{-7} \text{ erg}, \quad . \quad . \quad . \quad . \quad . \quad (28)$$

and according to (4) above, this is the 1/17·85 part of the total energy content of the negative electron. This would make the total energy of double ionization of the free hydrogen atom double this figure, since in the free atom the two electrons are supposedly symmetrical. The numerical value thus obtained is probably much too great, and the reason for giving it is to show that the contraction of the semi-minor axis is probably much less than from 1·065 down to 1×10^{-13} cm. as arbitrarily assumed. However, since the experimental value of this is unknown, it may be assumed without affecting any of the results that follow appreciably that $b = 10^{-13}$ cm. in round numbers, and that the eccentricity is 0·9547 in the free hydrogen atom as computed.

IV. *The Hydrogen Molecule.*

Let us first consider in a general preliminary way the formation of the hydrogen molecule by the uniting of two hydrogen atoms. The first striking result of an application of the equations expressing the forces which are given below is that the second atom exerts a very large force in one direction upon the two negative electrons of the atom, and a correspondingly large force upon the positive charge of the atom in the opposite direction. The effect of these larger forces is necessarily to change the pressure between the electrons and the positive charge as well as to displace very slightly the location of the positive charge to one side of the centre-line of the two electrons. These larger forces, in other words, have the effect of slightly deforming the atom itself, so that it is no longer a symmetrical atom as it exists in the free state. We really have to deal with a slightly different atom when it forms part of a molecule as well as during the process of formation of the molecule than when free.

It required some time and experience to realize that these deformations are of any practical importance, since they are evidently very small effects. The reason why they become important, when examined in terms of the equations expressing the electrostatic forces between the fundamental bodies, is because the asymmetry of the deformed atom introduces new terms in the lower orders of the distance between centres of the two atoms of the molecule, denoted by r. Recalling that the forces are necessarily expressed by an infinite series in terms of r^{-2}, r^{-3}, r^{-4}, etc., and remembering that the series is so rapidly convergent that each term is nearly 10^5 times smaller than the preceding term, unless some special condition is imposed upon the coefficients of the terms, it appears that ordinarily the first term of the series represents the sum of all its terms to a close approximation. When the two atoms are each symmetrical with respect to an axis and centre, it results that all the odd powers of r have vanishing coefficients in the series expressing the total electrostatic force of a second atom upon the first. And besides this, all coefficients vanish up to but not including the r^{-6} term. Hence the first term of the series is the r^{-6} term, which would represent practically the whole force unless its coefficient is modified by some condition connected with the form of the electron. The next term of this series for a symmetrical atom is the r^{-8} term, which is ordinarily 10^{10} times smaller than the r^5 term and is of no value.

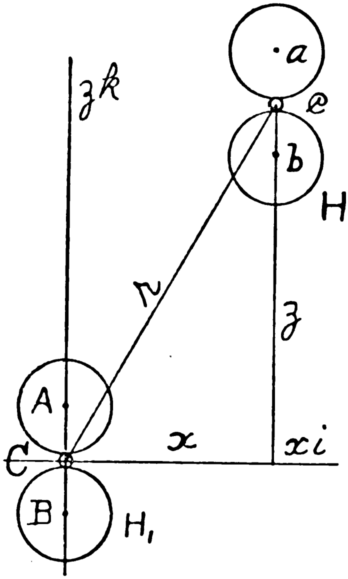
With a deformed atom, however, not only do earlier terms appear of lower orders in r, but the odd powers are present as well, the small coefficients of the earlier terms giving values that compare on equal terms with the important r^{-6} term above mentioned, and they are therefore not to be neglected.

This matter may be understood so much more readily when the equations referred to are before us that it seems best to give them at once, and they will be given in progressive steps of approximation to the model of the atom of fig. 1. It is regretted that there is not space to give all the details of their derivation; but to do this would not only extend the paper to great lengths, but might at the same time obscure the purpose and aims of the whole. So results only are given in this paper, but the processes are clearly indicated.

V. *The Spherical Electron in a Symmetrical Atom.*

As a beginning let it be supposed that each fundamental charge in the atom has a spherical shape, and that each atom is symmetrical with respect to its central point, in order that comparisons may be made later and the effect of non-spheres and asymmetry noted. A diagram of the atoms of the hydrogen molecule would then be represented as in fig. 2. Each charge may be treated mathematically as though it were all concentrated at the centre of its respective sphere. The centre of the first atom, H_1, composed of two negative electrons, A and B, and one positive charge, C, is located with its centre at the origin of coordinates, the z- or k-axis taking the polar and the x- or i-axis the equatorial direction. The centre of the second atom, H_2, is located in any general position at the point (x, z), but its axis, which in the final model is an axis of rotation for each fundamental body, is shown as parallel to that of the first atom, H_1, that is parallel to the z-axis.

Fig. 2.



Hydrogen molecule assuming spherical electrons.

The distance between the centres of A and C, B and C, a and c, and b and c may be denoted by b, which is very closely equal to the radius of the negative electron ; and the distance between the centre of the second atom, namely c, and the centre of the first, namely C, may be denoted by r.

The direction cosines defining the position of the centre of the second atom with respect to the first may be denoted by

$$X = x/r \quad \text{and} \quad Z = z/r. \quad . \quad . \quad . \quad . \qquad (29)$$

Then it may be shown that according to the inverse-square-law of electrostatic force, the force upon the positive charge $C=2e$ of the first atom due to the sum of the forces of both *a* and *b* of the second atom is given by the two components resolved along the *x*- and *z*-axes as follows:

$$\underset{a+b \text{ on C}}{F_x} = \frac{e^2}{k} X[4r^{-2} - 6b^2r^{-4}f_{x,4}(Z) + \tfrac{15}{2}b^4r^{-6}f_{x,6}(Z) \ldots], \quad (30)$$

$$F_z = \frac{e^2}{k} Z[4r^{-2} - 6b^2r^{-4}f_{z,4}(Z) + \tfrac{5}{2}b^4r^{-6}f_{z,6}(Z) \ldots], \quad (31)$$

where

$$f_{x,4} = 1 - 5Z^2, \quad \ldots \ldots \ldots \quad (32)$$

$$f_{z,4} = 3 - 5Z^2, \quad \ldots \ldots \ldots \quad (33)$$

$$f_{x,6} = 1 - 14Z^2 + 21Z^4, \quad \ldots \ldots \quad (34)$$

$$f_{z,6} = 15 - 70Z^2 + 63Z^4. \quad \ldots \ldots \quad (35)$$

When positive, these represent attractive forces.

The force upon the two negative electrons, A and B together, of the first atom due to the two, *a* and *b* together, of the second atom is given by

$$\underset{\substack{a+b \\ \text{on } A+B}}{F_x} = \frac{e^2}{k} X[-4r^{-2} + 12b^2r^{-4}f_{x,4}(Z) - 60b^4r^{-6}f_{x,6}(Z) \ldots], \quad \ldots \quad (36)$$

$$F_z = \frac{e^2}{k} Z[-4r^{-2} + 12b^2r^{-4}f_{z,4}(Z) - 20b^4r^{-6}f_{z,6}(Z) \ldots]. \quad \ldots \quad (37)$$

The force upon C of the first atom due to *c* of the second is simply

$$\underset{c \text{ on C}}{F_x} = \frac{e^2}{k} X(-4r^{-2}), \quad \ldots \ldots \quad (38)$$

$$F_z = \frac{e^2}{k} Z(-4r^{-2}). \quad \ldots \ldots \quad (39)$$

The force of the whole atom H_2 upon the positive charge C of the first atom is evidently the sum of (30) and (38) for the *x*-component, and of (31) and (39) for the *z*-component. It is not necessary to write this down, because the result is the same as (30) and (31) when the r^{-2} terms are omitted.

The force of the whole atom H_2 upon the two electrons A and B of the first atom is evidently the sum of (30) and (36) for the *x*-component, and of (31) and (37) for the *z*-component, since the force of *a* plus *b* upon C is evidently the same as that of c on A plus B. This sum is

$$\underset{\mathrm{H_2\ on\ A+B}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\mathrm{X}\left[6b^2r^{-4}f_{x,4}(\mathrm{Z})-\frac{105}{2}b^4r^{-6}f_{x,6}(\mathrm{Z})\ldots\right], \quad . \quad (40)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\mathrm{Z}\left[6b^2r^{-4}f_{z,4}(\mathrm{Z})-\frac{35}{2}b^4r^{-6}f_{z,6}(\mathrm{Z})\ldots\right], \quad . \quad (41)$$

where the Z-functions are given by (32) to (35) inclusive.

The force upon the whole first atom due to the second is then the sum of (30) and (40) for the x-component, and of (31) and (41) for the z-component, remembering to omit the r^{-2} terms of (30) and (31) as pointed out above. Hence we have

$$\underset{\mathrm{H_2\ on\ H_1}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\mathrm{X}\left[-45b^4r^{-6}f_{x,6}(\mathrm{Z})\ldots\right], \quad . \quad . \quad . \quad (42)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\mathrm{Z}\left[-15b^4r^{-6}f_{z,6}(\mathrm{Z})\ldots\right]. \quad . \quad . \quad . \quad (43)$$

The above equations illustrate some of the statements made above. First, because the atoms are symmetrical only the r^{-2}, r^{-4}, and r^{-6} terms of these series are present, the odd powers being absent because their coefficients vanish. Secondly, if numerical values are assigned to b and to r, making $b=10^{-13}$ cm. and $r=10^{-8}$ cm., we have

$$\frac{b^6r^{-8}}{b^4r^{-6}}=\frac{b^4r^{-6}}{b^2r^{-4}}=b^2r^{-2}=10^{-26+16}=10^{-10}. \quad . \quad . \quad (44)$$

And since the coefficients involving Z, which is always unity or less, are negligible by comparison, it is evident that each succeeding term of these series is of the order 10^{10} times smaller than the preceding term. That is to say, the first term of each represents approximately the whole force.

While the force of any single electron in the second atom upon any one in the first obeys the inverse-square law, yet the effect of the whole second atom upon any one electron in the first obeys the inverse-fourth-power law, see (40) and (41), and the whole second atom on the first obeys the inverse-sixth-power law, see (42) and (43). Hence there are no inverse square forces acting within any atom of this type because of any distant neutral atom. By far the largest forces acting because of the second or distant atom are the inverse-fourth-power of the distant forces, and these have no effect upon the atom to produce any translational motion, but they set up an internal strain within the atom itself. The translational force upon the whole atom follows the inverse-sixth-power of the distance law, but these forces are minute as compared with those producing the internal strain as shown, since an r^{-6} term is nearly 10^{10} times smaller than an r^{-4} term.

As a result of this investigation it becomes evident that the larger energy transformations, taking place when molecules are formed from free atoms that were previously at a great distance apart, follow in the wake of the larger forces concerned, and are therefore manifested in the internal strain set up within the atom. Evidently this energy is traceable to a change in the energy content of the electrons themselves. But it is not profitable to pursue this simplified type of atom any further, because equations (42) and (43) show that there can be no equilibrium position where the two atoms will stand in stable equilibrium at any distance. Subsequent terms in the higher powers of r are of no value, and no values of the two variables Z and r will reduce both the x- and the z-components, that is the total force, to zero.

At first thought, without giving the matter full consideration, one might have imagined that no equilibrium for a system of point charges of this kind should be expected because of the general theorem of Ernshaw. This theorem, however, can have no bearing on this problem, for the reason that another condition has been imposed in that the two axes of the atoms have been assumed to be parallel to each other in all positions. This result is brought about by the rotation of each fundamental charge upon its own axis, which gives rise to an electromagnetic force that is not contemplated by Ernshaw's theorem. It is this rotation that keeps the two axes parallel, but after that we are merely concerned with the electrostatic forces, and these are all that we have to investigate for reasons that have been clearly stated in the previously published papers cited.

VI. *The Circle-and-Point-Electrons in a Symmetrical Atom.*

In the historical order the next form of atom subjected to computation approaches the form of fig. 1 much closer than the assumption of simple spheres as above. But this new computation still assumes a perfectly symmetrical atom, and makes no allowance for any internal strain, and on this account in the light of subsequent experience it could not be expected to be entirely successful and satisfactory. Because the solution of the problem of finding the electrostatic force exerted upon one oblate spheroid of the kind above described due to a second one on the assumption of the inverse-square law as between the infinitesimal elements of charge supposed to be uniformly distributed throughout the volume of the spheroid has never been obtained, it has been necessary to approach the condition of the model of fig. 1 by the use of solutions which are available.

In the closer approximation to the spheroid of the electron the inscribed sphere is imagined to be cut out. This leaves a ring of charge thickest at the equator and tapering in thickness towards the poles. The total charge of the electron is thus divided mentally into the sum of two—a sphere and a ring. The sphere may be represented mathematically by a point at its centre, and the ring may be approximated by considering it as the equivalent of a circle of the proper radius, whose centre coincides with the centre of the spheroid and whose plane is the equatorial plane. The oblate-spheroid-electron is thus replaced for mathematical requirements by a circle-and-point-electron. The approximation is close, however, and the eccentricity of the spheroid is represented in the circle-and-point-electron. A change in the eccentricity of the spheroid changes the size of the inscribed sphere, and because the charges are proportional to their volumes, some of the charge switches over from the point to the circle and *vice versa* in the circle-and-point-electron.

Denoting by ρ the ratio of the charge on the circle to the whole charge of the electron e, it is easy to show * that ρ is equal to the square of the eccentricity of the spheroid, so that

$$\rho = \epsilon^2. \qquad (45)$$

The charge on the point is then

$$E_1 = (1-\rho)e, \qquad (46)$$

and the charge on the circle is

$$E_2 = \rho e, \qquad (47)$$

their sum being

$$E_1 + E_2 = e. \qquad (48)$$

The ratio ρ, like ϵ, is always less than unity, and as the form of the spheroid changes from a sphere to a very flat spheroid more and more charge shifts over from the point to the circle. For the sphere both ρ and ϵ are zero, and $E_1 = e$, while $E_2 = 0$. As ρ approaches unity, E_1 approaches zero and E_2 approaches e.

The electrostatic force of one spheroid upon another is thus simplified to depend upon the force of one circle upon another. Fortunately this latter is obtainable. It may be found from the equation giving the average force* exerted by one point charge revolving in a circle upon another point charge revolving in a different circle. The equation assumes, however, that the planes of the two circles are parallel.

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* *Loc. cit.* second paper, p. 907.

VII. *The Electrostatic Force of a Second Stationary Circle of Charge upon a First Stationary Circle of Charge with Parallel Planes.*

Since this equation is fundamental to any solution involving circles, it will be given in full for reference. The force is that of a secondary stationary circle of radius a_2 uniformly charged around its circumference by a total charge of E_2 acting upon a first circle of radius a_1 with its circumference uniformly charged to the amount E_1, their planes being parallel to each other. For brevity the sum of the squares of the radii of the two circles is denoted by

$$\sigma = a_2^2 + a_1^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (49)$$

and their product by

$$\delta = a_2 a_1 . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (50)$$

The three components of the force along the x-, y-, and z-axes are then as follows :—

$$\underset{\substack{\text{circle } a_2 \\ \text{on} \\ \text{circle } a_1}}{F_x} = \frac{E_1E_2}{k} X \Big[-r^{-2} + 3\sigma r^{-4} f_{x,4}(Z) - \tfrac{45}{8}(\sigma^2 + 2\delta^2) r^{-6} f_{x,6}(Z)$$
$$+ \tfrac{35}{4}\sigma(\sigma^2 + 6\delta^2) r^{-8} f_{x,8}(Z)$$
$$- \tfrac{1575}{128}(\sigma^4 + 12\delta^2\sigma^2 + 6\delta^4) r^{-10} f_{x,10}(Z) \ldots \Big], \quad . \qquad (51)$$

$$F_y = \frac{E_1E_2}{k} Y \text{ [same bracket as in (51)]}, \quad . \quad . \quad . \quad . \qquad (52)$$

$$F_z = \frac{E_1E}{k} Z \Big[-r^{-2} + \tfrac{1}{2} \times 3\sigma r^{-4} f_{z,4}(Z)$$
$$- \tfrac{1}{3} \times \tfrac{45}{8}(\sigma^2 + 2\delta^2) r^{-6} f_{z,6}(Z)$$
$$+ \tfrac{1}{4} \times \tfrac{35}{4}\sigma(\sigma^2 + 6\delta^2) r^{-8} f_{z,8}(Z)$$
$$- \tfrac{1}{5} \times \tfrac{1575}{128}(\sigma^4 + 12\delta^2\sigma^2 + 6\delta^4) r^{-10} f_{z,10}(Z) \ldots \Big],$$
$$. \quad . \quad . \quad . \qquad (53)$$

---

* Crehore, Phil. Mag. July 1913, equations (42) and (44), pp. 69 and 70. The sign of (44) should be changed to minus, due to a misprint. In giving the numerical values of the constants B on p. 70, the first column should read $B_{4,2} = 5B_{2,2}$; $B_{6,2} = \frac{7}{2}B_{4,2}$; $B_{8,2} = \frac{9}{3}B_{6,2}$; $B_{10,2} = \frac{11}{4}B_{8,2}$; $B_{12,2} = \frac{13}{5}B_{10,2}$; $B_{14,2} = \frac{15}{6}B_{12,2}$. This correction was noted on p. 325, Phil. Mag. Feb. 1915, footnote.

where

$$
\begin{aligned}
f_{x,4}(\mathrm{Z}) &= a_4 + b_4\mathrm{Z}^2,\\
f_{x,6}(\mathrm{Z}) &= a_6 + b_6\mathrm{Z}^2 + c_6\mathrm{Z}^4,\\
f_{x,8}(\mathrm{Z}) &= a_8 + b_8\mathrm{Z}^2 + c_8\mathrm{Z}^4 + d_8\mathrm{Z}^6,\\
f_{x,10}(\mathrm{Z}) &= a_{10} + b_{10}\mathrm{Z}^2 + c_{10}\mathrm{Z}^4 + d_{10}\mathrm{Z}^6 + e_{10}\mathrm{Z}^8\,; \quad . \quad . \quad . \qquad (54)
\end{aligned}
$$

and

$$
\begin{aligned}
f_{z,4}(\mathrm{Z}) &= 6(a_4 + \tfrac{1}{3}b_4\mathrm{Z}^2),\\
f_{z,6}(\mathrm{Z}) &= 15(a_6 + \tfrac{1}{3}b_6\mathrm{Z}^2 + \tfrac{1}{5}c_6\mathrm{Z}^4),\\
f_{z,8}(\mathrm{Z}) &= 28(a_8 + \tfrac{1}{3}b_8\mathrm{Z}^2 + \tfrac{1}{5}c_8\mathrm{Z}^4 + \tfrac{1}{7}d_8\mathrm{Z}^6),\\
f_{z,10}(\mathrm{Z}) &= 45(a_{10} + \tfrac{1}{3}b_{10}\mathrm{Z}^2 + \tfrac{1}{5}c_{10}\mathrm{Z}^4 + \tfrac{1}{7}d_{10}\mathrm{Z}^6 + \tfrac{1}{9}e_{10}\mathrm{Z}^8)\,; \quad . \qquad (55)
\end{aligned}
$$

and where the numerics a, b, c, d, and e have the following values:

$$
\begin{array}{llll}
a_4 = -\frac{1}{4}\,; & a_6 = \frac{1}{8}\,; & a_8 = -\frac{5}{64}\,; & a_{10} = \frac{7}{128}\,;\\
b_4 = \frac{5}{4}\,; & b_6 = -\frac{7}{4}\,; & b_8 = \frac{135}{64}\,; & b_{10} = -\frac{77}{32}\,;\\
 & c_6 = \frac{21}{8}\,; & c_8 = -\frac{495}{64}\,; & c_{10} = \frac{1001}{64}\,;\\
 & & d_8 = \frac{429}{64}\,; & d_{10} = -\frac{1001}{32}\,;\\
 & & & e_{10} = \frac{2431}{128}\,. \quad . \qquad (56)
\end{array}
$$

The functions of Z given by (54) and (55) are not exactly the same as those given in (32) to (35), but they are multiples of them. The expression for the force has been developed to include the inverse tenth power of the distance r, but we shall not have occasion to make use of it for the purposes of this paper beyond the inverse sixth term. By means of this equation the total force of a second circle-and-point-electron acting upon a first such electron may be written down. The force of a circle upon a point charge may be obtained from this by making either radius a_2 or a_1 as the case may be equal to zero, and at the same time taking care that the proper charges are used for each body. The whole force of a second electron upon a first is thus the sum of four component parts—the force of the circle of the second on that of the first, the force of the point of the second on the circle of the first, the force of the circle of the second on the point of the first, and, lastly, the force of the point of the second upon the point of the first.

VIII. *The Electrostatic Force of a Second Circle-and-Point-Electron upon a First.*

Without giving each of these component parts above mentioned separately, the whole force of a second circle-and-point-electron of charge $-e$, radius a_2 and ratio of charge on the circle to the total charge, ρ_2, acting upon a first electron of the same charge but having different values of a and ρ denoted by a_1 and ρ_1, is as follows :—

$$\underset{\substack{\text{Second elec.}\\ \text{on a}\\ \text{First elec.}}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\mathrm{X}\left[-r^{-2}+\mathrm{A}r^{-4}f_{x,4}(\mathrm{Z})+\mathrm{B}r^{-6}f_{x,6}(\mathrm{Z}) + \mathrm{C}r^{-8}f_{x,8}(\mathrm{Z})+\mathrm{D}r^{-10}f_{x,10}(\mathrm{Z})\ldots\right], \quad (57)$$

$$\mathrm{F}_y = \frac{e^2}{\mathrm{k}}\mathrm{Y}\,[\text{same bracket as in (57)}], \quad (58)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\mathrm{Z}\left[-r^{-2}+\tfrac{1}{2}\mathrm{A}r^{-4}f_{z,4}(\mathrm{Z})+\tfrac{1}{3}\mathrm{B}r^{-6}f_{z,6}(\mathrm{Z}) + \tfrac{1}{4}\mathrm{C}r^{-8}f_{z,8}(\mathrm{Z})+\tfrac{1}{5}\mathrm{D}r^{-10}f_{z,10}(\mathrm{Z})\ldots\right], \quad (59)$$

where

$$\mathrm{A}=3(\rho_2a_2{}^2+\rho_1a_1{}^2), \quad (60)$$

$$\mathrm{B}=-\tfrac{45}{8}(4\rho_2\rho_1a_2{}^2a_1{}^2+\rho_2a_2{}^4+\rho_1a_1{}^4), \quad (61)$$

$$\mathrm{C}=\tfrac{35}{4}[9\rho_2\rho_1a_2{}^2a_1{}^2(a_2{}^2+a_1{}^2)+\rho_2a_2{}^6+\rho_1a_1{}^6], \quad (62)$$

$$\mathrm{D}=-\tfrac{1575}{128}(16\rho_2\rho_1a_2{}^2a_1{}^6+36\rho_2\rho_1a_2{}^4a_1{}^4 + 16\rho_2\rho_1a_2{}^6a_1{}^2+\rho_2a_2{}^8+\rho_1a_1{}^8), \quad (63)$$

and where the functions of Z are the same as given in (54) and (55).

IX. *The Symmetrical Atom Form of Molecule.*

These fundamental equations may be used to obtain the force upon a first atom situated at the origin of coordinates due to a second atom in any general position (x, y) in a manner similar to the process employed above with spherical electrons. Only the results of these operations can be given here, but they have been carefully checked until we are assured of their accuracy upon the premises, namely their dependence upon their fundamental equations (57) to (59). These equations hold good for different kinds of electrons, those differing in a and ρ, but we shall now consider first the case where all electrons are alike and where the atom is a symmetrical structure, the centres of the three bodies A, B, and C being in one line, and the distances AC, BC, ac, and bc each equal to b, the semi-minor axis of the negative electron. Fig. 3 represents two such circle-and-point-electron atoms forming the molecule. The circles viewed on edge appear as lines.

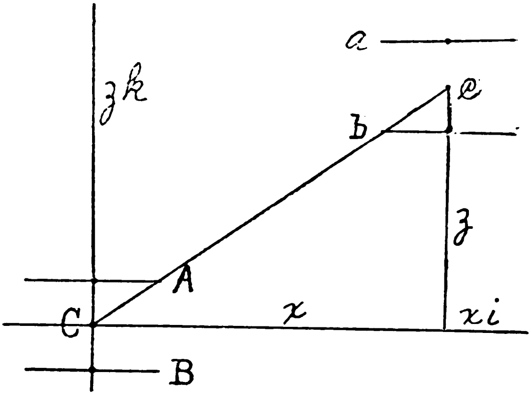
The force of the atom H_2 upon the positive charge alone, namely C, is as follows :—

$$\underset{H_2 \text{ on } C}{F_x} = \frac{e^2}{k} X\Big[-6(b^2 - \tfrac{1}{2}\rho a^2) r^{-4} f_{x,4}(Z) \\ + \tfrac{15}{4}(2b^4 - 6b^2\rho a^2 + \tfrac{3}{4}\rho a^4) r^{-6} f_{x,6}(Z) \ldots\Big], \qquad (64)$$

$$F_z = \frac{e^2}{k} Z\Big[-6(b^2 - \tfrac{1}{2}\rho a^2) r^{-4} f_{z,4}(Z) \\ + \tfrac{5}{4}(2b^4 - 6b^2\rho a^2 + \tfrac{3}{4}\rho a^4) r^{-6} f_{z,6}(Z) \ldots\Big], \quad . \qquad (65)$$

where the functions of Z are as in (32) to (35).

Fig 3.



Hydrogen molecule with symmetrical atoms using circle-and-point electrons.

If ρ is put equal to zero in these expressions, it is equivalent to assuming that the electrons are spherical as before stated. When this is done (64) becomes identical with (30) and (65) with (31) after omitting the r^{-2} terms as before explained. So the result in these last equations is more general, including the former as a special case. The lowest order term, as before, is the r^{-4} term, and only even powers of r are present, because the atom is still assumed symmetrical and undeformed. The value of the force now, however, is completely altered, since it depends upon the relative values of b^2 and $\frac{1}{2}\rho a^2$. If these quantities were equal to each other the r^{-4} term would vanish entirely. Unless they are so closely equal that their difference is approximately 10^{10} times smaller than either term alone, then the r^{-4} term is far greater than the r^{-6} term, and it represents therefore the whole force. The numerical value of this quantity, which may be denoted by P, namely

$$P = b^2 - \tfrac{1}{2}\rho a^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (66)$$

is

$$P = -1{\cdot}25 \times 10^{-26}\ \text{cm.}^2. \quad . \quad . \quad . \qquad (67)$$

In order not to interrupt the continuity of the presentation, the derivation of this numerical value for P is given in Appendix A to this paper. The second term of (66) is greater than the first, and the total greater than b^2 alone, but with the opposite sign. The value of b^2 alone is 10^{-26} cm.^{2} Hence the r^{-4} terms of (64) and (65) are by far the greatest.

The force upon the two electrons A and B together due to the second atom is given by

$$\underset{\substack{\text{H}_2\text{ on}\\ \text{A+B}}}{F_x} = \frac{e^2}{k} X[6Pr^{-4}f_{x,4}(Z) - \tfrac{15}{4}(14b^4 - 18b^2\rho a^2 + 3\rho^2 a^4 + \tfrac{3}{4}\rho a^4)r^{-6}f_{x,6}(Z) \ldots], \quad . \quad . \qquad (68)$$

$$F_z = \frac{e^2}{k} Z[6Pr^{-4}f_{z,4}(Z) - \tfrac{5}{4}(14b^4 - 18b^2\rho a^2 + 3\rho^2 a^4 + \tfrac{3}{4}\rho a^4)r^{-6}f_{z,6}(Z) \ldots], \quad . \quad . \qquad (69)$$

and here also the r^{-4} terms are by far the largest of the series, but it is to be observed that the r^{-4} terms of the force on the two electrons in (68) or (69) are exactly equal and opposite to the r^{-4} terms respectively of the force upon the positive charge of (64) and (65). These large forces drop out when the sum is taken to obtain the force of the second atom upon the first which follows.

$$\underset{\text{H}_2\text{ on H}_1}{F_x} = \frac{e^2}{k} X[-45P^2 r^{-6} f_{x,6}(Z) \ldots], \quad . \quad . \quad . \qquad (70)$$

$$F_z = \frac{e^2}{k} Z[-15P^2 r^{-6} f_{z,6}(Z) \ldots], \quad . \quad . \quad . \qquad (71)$$

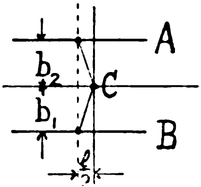
where P is given in (67), and the functions of Z in (34) and (35). This same equation developed to include the r^{-8} and r^{-10} terms is given as equation (17), p. 1029, Phil. Mag. for June 1922. An attempt was made in that paper to obtain an equilibrium by means of this symmetrical atom, using the r^{-6}, r^{-8}, and r^{-10} terms and taking P as an unknown quantity to which different numerical values might be assigned. In the r^{-6} term the square of P occurs as a factor, while in the r^{-8} term the first power of P is a factor, and in the r^{-10} term it is not a factor. But to obtain any equilibrium a value of P must be chosen such as to render the magnitudes of the three terms of the same order. Such a value was found in the neighbourhood of 7×10^{-35} for P, which requires that the two terms of (66) shall be equal to each other to a very exact degree. This in itself seems improbable. Moreover, the forces with such a small value for P are much too small, each term being of the order $\frac{e^2}{\text{k}} 10^{-22}$ dyne near the position of equilibrium. And again, the law of force between the atoms of a solid body would then appear to be higher than the inverse-sixth power of the distance, which is not supported by experimental evidence. Such evidence indicates that the variation of the force with the distance obeys the inverse-fifth power of the distance law nearer than any other.

On the other hand the symmetrical and undeformed atom of fig. 2 with spheres offers no possibility of forming a molecule with two such atoms at a distance of the order of 10^{-8} cm., while the atom of fig. 3 with circle-and-point-electrons shows that such a thing is quite possible, and this in itself seemed an important result. But a further study of the problem has shown that the former attempt to obtain an equilibrium in the paper referred to is open to the objection above mentioned, and these objections have all been removed by the subsequent development. The part played by the comparatively large forces expressed by the r^{-4} terms in (68) and (69) cannot be neglected, because the energy changes that take place as the molecule is being formed are necessarily connected with these larger forces; but these are manifested only within the atom itself, and produce an internal strain. When these strains are taken into the account the problem becomes much enlarged in scope and more complex, but if this is the truth of the matter the situation must be faced.

X. *The Unsymmetrical and Deformed Atom.*

The effect of the x-component of the force of the second atom upon the positive charge and upon the two electrons of the first atom is to pull the one to the right and the other to the left, thus very slightly displacing the positive charge off from the line joining the centres of the two electrons, as illustrated in fig. 4. The sum of these displacements in the two atoms of a molecule may be denoted by l, while $l/2$ denotes that in the single atom of fig. 4. The magnitude of the displacement will be shown to be less than the radius of the positive charge itself, and in order to show it in the figure it has been greatly magnified. Circle-and-point-electrons are illustrated in the figure, but it should be kept in mind that the electrons are oblate spheroids in contact with the positive charge.

Fig. 4.

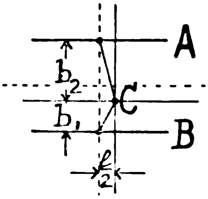


Hydrogen atom with circle-and-point electrons illustrating the. x-displacement.

The effect of the z-component of the force is to increase the pressure between an electron, say B, and the positive charge, and to lessen the pressure between the other electron, A, and the positive charge. This increases the area of the one electron, B, and reduces slightly its minor axis, and decreases the area of A, increasing its minor axis, but not necessarily by the same amount as that of B was increased, since the force of the second atom upon A differs slightly from that upon B on account of their different distances.

Fig. 5 represents the effect of the z-component of the

Fig. 5.



Hydrogen atom illustrating both the x- and z-displacements.

force upon H_1 together with that of the x-component. The vertical distance from A to C has increased from b in fig. 3 to b_2 in fig. 5, while that from B to C has diminished from b to b_1. It is conceivable that the minor axis of A increases by just the same amount as that of B decreases, in which case the vertical distance from A to B would remain unchanged. But when the axis of A increases, this electron performs work giving up some of its energy content, and similarly, when the axis of B decreases, work must be done upon it to increase its surface, and it consequently absorbs energy. If the amounts of the increase of the axis of A and the decrease of that of B were the same, then all of the energy given up by A would be reabsorbed by B, and there would occur no total change in the energy content of the atom. As long, therefore, as the vertical distance from the centre of A to that of B remains the same as it was in the free atom, so long does the energy of the whole atom remain unchanged. But if the distance AB increases over and above its value in the free atom, then work has been done by the atoms in forming the molecule at the expense of some of the energy content of the electrons as they existed in the free atoms. Since it is true that work must be done by outside influences to separate the molecule of hydrogen into free atoms and thus restore the two electrons of an atom to the condition they have in free atoms, it may be concluded that the distance AB must be slightly greater when the atom forms part of a molecule than when the atom is free. This means also that the over-all axial distance from the top surface of A to the bottom surface of B in fig. 1 must be slightly greater in the molecule than in the free atom.

XI. *The Energy of Dissociation of the Hydrogen Molecule.*

Let it be supposed, therefore, that the semi-minor axis of A increases from b to b_2 and that of B decreases from b to b_1, so that the change in that of A is b_2-b and in that of B, b_1-b; then, according to (26) above, the change in their respective energy contents is:

$$\text{For A,}\quad \Delta E_A = -6{\cdot}964\times10^6(b_2-b), \quad . \quad . \quad . \quad (72)$$

$$\text{and for B,}\quad \Delta E_B = -6{\cdot}964\times10^6(b_1-b). \quad . \quad . \quad . \quad (73)$$

The sum of these two energies represents the work done by the atom in forming the molecule, and is

$$\Delta E_A + \Delta E_B = -6{\cdot}964\times10^6[(b_2+b_1)-2b], \quad . \quad (74)$$

which must be negative as representing a loss of energy content on the whole. Now $2(b_2+b_1)$ is the polar diameter of the atom when in the molecule, and $4b$ its diameter when free; so that it is evident that the new diameter must be greater than the free diameter. This neglects the very small diameter of the positive charge of the order of 10^{-16} cm., which cancels any way in subtracting.

The new semi-minor axis of A may then be expressed as

$$b_2 = b+a+h, \quad . \quad . \quad . \quad . \quad . \quad (75)$$

and of B,

$$b_1 = b-a, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (76)$$

where a now represents the major part of the change in the semi-minor axis as the molecule is formed, and h represents the very small excess of change of electron A over that of B. From this we find that

$$b_2-b_1 = 2a+h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (77)$$

$$\text{and} \quad b_2+b_1 = 2b+h,$$

$$\text{or} \quad h = (b_2+b_1)-2b\,; \quad . \quad . \quad . \quad (78)$$

and so by (74) h is not only proportional to the whole work done in forming the molecule, but it also represents half the difference between the new and old polar diameters of the atom.

Using the experimental value of the energy of dissociation of the hydrogen molecule (Langmuir) as $5 \cdot 8 \times 10^{-12}$ erg, and one-half of this as the energy change per atom, we have from (74)

$$\Delta E = -\frac{5 \cdot 8}{2} 10^{-12} = \Delta E_A + \Delta E_B = -6 \cdot 964 \times 10^6 h, \quad (79)$$

whence the value of h becomes known numerically as

$$h = \frac{5 \cdot 8}{2 \times 6 \cdot 964} 10^{-18} = \frac{58}{13 \cdot 928} 10^{-19} = 4 \cdot 164 \times 10^{-19} \text{ cm.} \quad . \quad . \quad . \quad (80)$$

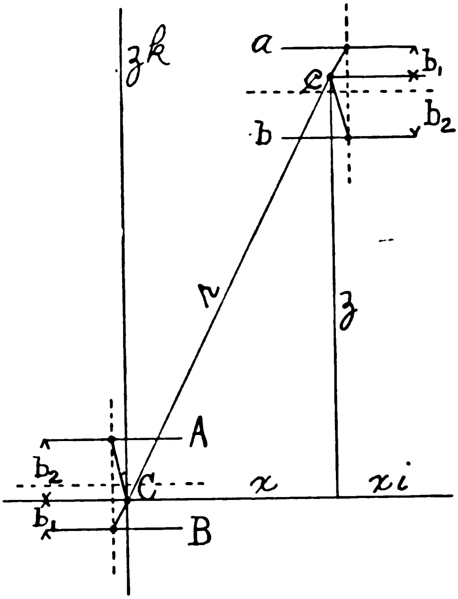
This is its value at the point of equilibrium of the two atoms when in the molecule, and is about 1/240,000th part of the semi-minor axis of the electron itself. The principal change in the minor axis is, however, greater than h; that is to say, the a of (75) and (76) is considerably larger than h.

XII. *The Forces acting upon the Individual Bodies of the First Atom of the Deformed Molecule.*

The complication that arises when allowance is made for the internal stresses within the atom itself as the molecule is formed is due to the circumstance that there is no longer a fixed atom that may be moved about from place to place, as there was in the cases above considered and illustrated by figs. 2 and 3, but the atom itself now changes with each new position. Instead of having but two variables to manage as in (70) and (71) above, the Z and the r, there are now five variables, namely Z, r, l, b_2, and b_1, all of which change with the relative positions of the atoms.

The resulting equations obtained with two such variable atoms, such as represented in fig. 5, and also shown as a molecule in fig. 6, will now be given in full without the rather laborious detail of their derivation. The principles of the operations as depending only upon electrostatic forces in the circle-and-point-electron approximation to the oblate spheroid have been fully explained above, and the work has been carefully checked, so that it is believed that the resulting equations are trustworthy as depending upon these premises.

Fig. 6.



The hydrogen molecule with deformed or strained atoms.

The force upon the positive charge, C, of the atom H_1 due to the two electrons only, a and b of the second atom, is given in (81) and (92) for the x- and the z-components of the force respectively up to and including the r^{-6} term. The force of the whole atom, H_2, upon C is found from this by adding the force of the positive charge, c upon C, which comes to the same thing as omitting the r^{-2} terms from (81) and (92), and hence this need not be written down again. The same thing occurred before in discussing equations (30) and (31) in the simpler case of the spherical electrons.

The equations that follow are complete, including the r^{-6} term, no terms having been omitted in the development, and are given for reference, although it will appear subsequently that they may be greatly simplified by omitting certain terms as unimportant when numerical values are introduced.

$$\begin{aligned}\underset{a+b\text{ on C}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\Big\{ & 4\mathrm{X}r^{-2} - 2\left[(2-3\mathrm{Z}^2)l - 3\mathrm{XZD}\right]r^{-3} \\ & + \Big[\tfrac{3}{2}(2-5\mathrm{Z}^2)\mathrm{X}l^2 - 3(4-5\mathrm{Z}^2)\mathrm{Z}l\mathrm{D} \\ & \quad - 3(1-5\mathrm{Z}^2)\mathrm{X}\left[(b_2{}^2+b_1{}^2) - \tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\right]\Big]r^{-4} \\ & + \Big[-\tfrac{1}{4}l^3f_0(\mathrm{Z}) + \tfrac{15}{4}l^2\mathrm{D}\,f_1(\mathrm{Z}) \\ & \quad + \tfrac{3}{2}l\left[(b_2{}^2+b_1{}^2) - \tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\right]f_2(\mathrm{Z}) \\ & \quad - 5\left[(b_2{}^3-b_1{}^3) - \tfrac{3}{2}(b_2\rho_2a_2{}^2 - b_1\rho_1a_1{}^2)\right]f_3(\mathrm{Z})\Big]r^{-5} \\ & + \Big[\tfrac{5}{4}\mathrm{X}l^4f_4(\mathrm{Z}) - \tfrac{15}{8}\mathrm{Z}l^3\mathrm{D}f_5(\mathrm{Z}) \\ & \quad - \tfrac{15}{8}\mathrm{X}l^2\left[(b_2{}^2+b_1{}^2) - \tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\right]f_6(\mathrm{Z}) \\ & \quad + \tfrac{5}{2}\mathrm{Z}l\left[(b_2{}^3-b_1{}^3) - \tfrac{3}{2}(b_2\rho_2a_2{}^2 - b_1\rho_1a_1{}^2)\right]f_7(\mathrm{Z}) \\ & \quad + \tfrac{15}{4}\mathrm{X}\Big[(b_2{}^4+b_1{}^4) - 3(b_2{}^2\rho_2a_2{}^2 + b_1{}^2\rho_1a_1{}^2) \\ & \quad + \tfrac{3}{8}(\rho_2a_2{}^4+\rho_1a_1{}^4)\Big]f_8(\mathrm{Z})\Big]r^{-6}\ldots\Big\}, \quad . \quad . \quad . \quad (81)\end{aligned}$$

where

$$f_0(\mathrm{Z}) = 8-40\mathrm{Z}^2+35\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (82)$$

$$f_1(\mathrm{Z}) = (4-7\mathrm{Z}^2)\mathrm{XZ}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (83)$$

$$f_2(\mathrm{Z}) = 4-35\mathrm{Z}^2+35\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (84)$$

$$f_3(\mathrm{Z}) = (3-7\mathrm{Z}^2)\mathrm{XZ}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (85)$$

$$f_4(\mathrm{Z}) = 1-7\mathrm{Z}^2+\tfrac{63}{8}\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (86)$$

$$f_5(\mathrm{Z}) = 8-28\mathrm{Z}^2+21\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (87)$$

$$f_6(\mathrm{Z}) = 4-49\mathrm{Z}^2+63\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (88)$$

$$f_7(\mathrm{Z}) = 18-77\mathrm{Z}^2+63\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (89)$$

$$f_8(\mathrm{Z}) = 1-14\mathrm{Z}^2+21\mathrm{Z}^4, \quad . \quad . \quad . \quad . \quad . \quad (90)$$

and $$\mathrm{D} = b_2-b_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$$

$$
\begin{aligned}
\underset{a+b\text{ on }C}{F_z} = \frac{\epsilon^2}{k}\Big\{ & 4Zr^{-2} - 2[3XZl + (1-3Z^2)D]r^{-3} \\
& + \big[\tfrac{3}{2}(4-5Z^2)Zl^2 + 3(1-5Z^2)XlD \\
& \quad - 3(3-5Z^2)Z[(b_2^2+b_1^2) - \tfrac{1}{2}(\rho_2 a_2^2 + \rho_1 a_1^2)]\big]r^{-4} \\
& + \big[-\tfrac{5}{4}l^3 f_1(Z) - \tfrac{3}{4}l^2 D f_2(Z) \\
& \quad + \tfrac{15}{2}l[(b_2^2+b_1^2) - \tfrac{1}{2}(\rho_2 a_2^2 + \rho_1 a_1^2)]f_3(Z) \\
& \quad + [(b_2^3 - b_1^3) - \tfrac{3}{2}(b_2\rho_2 a_2^2 - b_1\rho_1 a_1^2)]f_9(Z)\big]r^{-5} \\
& + \big[\tfrac{15}{32}l^4 Z f_5(Z) + \tfrac{5}{8}l^3 DX f_6(Z) \\
& \quad - \tfrac{15}{8}l^2 Z[(b_2^2+b_1^2) - \tfrac{1}{2}(\rho_2 a_2^2 + \rho_1 a_1^2)]f_7(Z) \\
& \quad - \tfrac{15}{2}lX[(b_2^3 - b_1^3) - \tfrac{3}{2}(b_2\rho_2 a_2^2 - b_1\rho_1 a_1^2)]f_8(Z) \\
& \quad + \tfrac{5}{4}Z[(b_2^4 + b_1^4) - 3(b_2^2\rho_2 a_2^2 + b_1^2\rho_1 a_1^2) \\
& \quad + \tfrac{3}{5}(\rho_2 a_2^4 + \rho_1 a_1^4)]f_{10}(Z)\big]r^{-6}\ldots\ldots\Big\}, \quad . \quad (92)
\end{aligned}
$$

where

$$f_9(Z) = 3 - 30Z^2 + 35Z^4 \quad . \quad . \quad . \quad . \quad (93)$$

and

$$f_{10}(Z) = 15 - 70Z^2 + 63Z^4, \quad . \quad . \quad . \quad . \quad (94)$$

the other functions of Z being as given in (82) to (90).

The force upon the two electrons A and B together of the first atom due to the two electrons *a* and *b* together of the second atom is given by (95) and (96), which follow.

$$
\begin{aligned}
\underset{\substack{a+b\text{ on}\\ A+B}}{F_x} = \frac{\epsilon^2}{k}\Big\{ & -4Xr^{-2} + 4[(2-3Z^2)l - 3XZD]r^{-3} \\
& + \big[-6(2-5Z^2)Xl^2 + 12(4-5Z^2)ZlD \\
& \quad + 3(1-5Z^2)X[2(b_2^2+b_1^2) - (\rho_2 a_2^2 + \rho_1 a_1^2) + D^2]\big]r^{-4} \\
& + \big[2l^3 f_0(Z) - 30l^2 D f_1(Z) - 3l[2(b_2^2+b_1^2) \\
& \quad - (\rho_2 a_2^2 + \rho_1 a_1^2) + D^2]f_2(Z) + 5[D^3 + 4(b_2^3 - b_1^3) \\
& \quad - 3(b_2\rho_2 a_2^2 - b_1\rho_1 a_1^2) - \tfrac{3}{2}(\rho_2 a_2^2 + \rho_1 a_1^2)D]f_3(Z)\big]r^{-5} \\
& + \big[-20Xl^4 f_4(Z) + 30Zl^3 D f_5(Z) \\
& \quad + \tfrac{15}{2}Xl^2[D^2 + 2(b_2^2+b_1^2) - (\rho_2 a_2^2 + \rho_1 a_1^2)]f_6(Z) \\
& \quad - 5Zl[D^3 + 4(b_2^3 - b_1^3) - 3(b_2\rho_2 a_2^2 - b_1\rho_1 a_1^2) \\
& \quad - \tfrac{3}{2}(\rho_2 a_2^2 + \rho_1 a_1^2)D]f_7(Z) \\
& \quad - \tfrac{15}{4}X[D^4 + 8(b_2^4 + b_1^4) + \tfrac{3}{4}(\rho_2 a_2^2 + \rho_1 a_1^2)^2 \\
& \quad + \tfrac{3}{4}(\rho_2 a_2^4 + \rho_1 a_1^4) - 3(\rho_2 a_2^2 + \rho_1 a_1^2)D^2 \\
& \quad - 12(b_2^2\rho_2 a_2^2 + b_1^2\rho_1 a_1^2)]f_8(Z)\big]r^{-6}\ldots\Big\}. \quad . \quad . \quad (95)
\end{aligned}
$$

$$
\begin{aligned}
\underset{\substack{a+b \text{ on}\\ \text{A}+\text{B}}}{\mathrm{F}_z} = \frac{e^2}{\mathrm{k}} \{ & -4\mathrm{Z}r^{-2}+4[3\mathrm{XZ}l+(1-3\mathrm{Z}^2)\mathrm{D}]r^{-3} \\
& +[-6(4-5\mathrm{Z}^2)\mathrm{Z}l^2-12(1-5\mathrm{Z}^2)\mathrm{X}l\mathrm{D} \\
& \quad +3(3-5\mathrm{Z}^2)\mathrm{Z}[2(b_2^2+b_1^2)-(\rho_2a_2^2+\rho_1a_1^2)+\mathrm{D}^2]]r^{-4} \\
& +[10l^3f_1(\mathrm{Z})+6l^2\mathrm{D}f_2(\mathrm{Z})-15l[2(b_2^2+b_1^2) \\
& \quad -(\rho_2a_2^2+\rho_1a_1^2)+\mathrm{D}^2]f_3(\mathrm{Z})-[\mathrm{D}^3+4(b_2^3-b_1^3) \\
& \quad -3(b_2\rho_2a_2^2-b_1\rho_1a_1^2)-\tfrac{3}{2}(\rho_2a_2^2+\rho_1a_1^2)\mathrm{D}]f_9(\mathrm{Z})]r^{-5} \\
& +[-\tfrac{15}{2}\mathrm{Z}l^4f_5(\mathrm{Z})-10\mathrm{X}l^3\mathrm{D}f_6(\mathrm{Z}) \\
& \quad +\tfrac{15}{2}\mathrm{Z}l^2[\mathrm{D}^2+2(b_2^2+b_1^2)-(\rho_2a_2^2+\rho_1a_1^2)]f_7(\mathrm{Z}) \\
& \quad +15\mathrm{X}l[\mathrm{D}^3+4(b_2^3-b_1^3)-3(b_2\rho_2a_2^2-b_1\rho_1a_1^2) \\
& \quad -\tfrac{3}{2}(\rho_2a_2^2+\rho_1a_1^2)\mathrm{D}]f_8(\mathrm{Z}) \\
& \quad -\tfrac{5}{4}\mathrm{Z}[\mathrm{D}^4+8(b_2^4+b_1^4)+\tfrac{3}{4}(\rho_2a_2^2+\rho_1a_1^2)^2 \\
& \quad +\tfrac{3}{4}(\rho_2a_2^4+\rho_1a_1^4)-3(\rho^2a_2^2+\rho_1a_1^2)\mathrm{D}^2 \\
& \quad -12(b_2^2\rho_2a_2^2+b_1^2\rho_1a_1^2)]f_{10}(\mathrm{Z})]r^{-6}\ldots\}, \quad . \quad . \quad (96)
\end{aligned}
$$

where the functions of Z are given by (82) to (94) above.

The force of the whole atom, H_2, upon the two electrons A and B together of the first atom is merely the sum of (81) and (95) for the x-component, and of (92) and (96) for the z-component, because the force of the positive charge, c, upon A and B together is exactly the same as that of a and b together upon the positive charge C. These sums are given by (97) and (98), which follow.

$$
\begin{aligned}
\underset{\substack{\mathrm{H}_2 \text{ on}\\ \text{A}+\text{B}}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}} \{ & 2[(2-3\mathrm{Z}^2)l-3\mathrm{XZD}]r^{-3} \\
& +[-\tfrac{9}{2}(2-5\mathrm{Z}^2)\mathrm{X}l^2+9(4-5\mathrm{Z}^2)\mathrm{Z}l\mathrm{D} \\
& \quad +3(1-5\mathrm{Z}^2)\mathrm{X}[(b_2^2+b_1^2)-\tfrac{1}{2}(\rho_2a_2^2+\rho_1a_1^2)+\mathrm{D}^2]]r^{-4} \\
& +[\tfrac{7}{4}l^3f_0(\mathrm{Z})-\tfrac{105}{4}l^2\mathrm{D}f_1(\mathrm{Z})-\tfrac{9}{2}l[(b_2^2+b_1^2) \\
& \quad -\tfrac{1}{2}((\rho_2a_2^2+\rho_1a_1^2)+\tfrac{2}{3}\mathrm{D}^2]f_2(\mathrm{Z})+5[\mathrm{D}^3+3(b_2^3-b_1^3) \\
& \quad -\tfrac{3}{2}(b_2\rho_2a_2^2-b_1\rho_1a_1^2)-\tfrac{3}{2}(\rho_2a_2^2+\rho_1a_1^2)\mathrm{D}]f_3(\mathrm{Z})]r^{-5} \\
& +[-\tfrac{75}{4}\mathrm{X}l^4f_4(\mathrm{Z})+\tfrac{225}{8}\mathrm{Z}l^3\mathrm{D}f_5(\mathrm{Z})+\tfrac{105}{8}\mathrm{X}l^2[(b_2^2+b_1^2) \\
& \quad -\tfrac{1}{2}(\rho_2a_2^2+\rho_1a_1^2)+\tfrac{4}{7}\mathrm{D}^2]f_6(\mathrm{Z})-5\mathrm{Z}l[\mathrm{D}^3+\tfrac{7}{2}(b_2^3-b_1^3) \\
& \quad -\tfrac{9}{4}(b_2\rho_2a_2^2-b_1a_1\rho_1^2)-\tfrac{3}{2}(\rho_2a_2^2+\rho_1a_1^2)\mathrm{D}]f_7(\mathrm{Z}) \\
& \quad -\tfrac{15}{4}\mathrm{X}[\mathrm{D}^4+7(b_2^4+b_1^4)+\tfrac{3}{4}(\rho_2a_2^2+\rho_1a_1^2)^2 \\
& \quad +\tfrac{3}{8}(\rho_2a_2^4+\rho_1a_1^4)-3(\rho_2a_2^2+\rho_1a_1^2)\mathrm{D}^2 \\
& \quad -9(b_2^2\rho_2a_2^2+b_1^2\rho_1a_1^2)]f_8(\mathrm{Z})]r^{-6}\ldots\}. \quad . \quad . \quad . \quad (97)
\end{aligned}
$$

$$
\begin{aligned}
\underset{\substack{\mathrm{H_2\ on}\\ \mathrm{A+B}}}{\mathrm{F}_z} = \frac{e^2}{\mathrm{k}}\Big\{ & 2\big[3\mathrm{XZ}l + (1-3\mathrm{Z}^2)\mathrm{D}\big]r^{-3} \\
& + \big[-\tfrac{9}{2}(4-5\mathrm{Z}^2)\mathrm{Z}l^2 - 9(1-5\mathrm{Z}^2)\mathrm{X}l\mathrm{D} \\
& \quad + 3(3-5\mathrm{Z}^2)\,\mathrm{Z}\big[(b_2{}^2+b_1{}^2) - \tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2) + \mathrm{D}^2\big]\big]r^{-4} \\
& + \big[\tfrac{35}{4}l^3f_1(\mathrm{Z}) + \tfrac{21}{4}l^2\mathrm{D}f_2(\mathrm{Z}) - \tfrac{45}{2}l\big[(b_2{}^2+b_1{}^2) \\
& \quad - \tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2) + \tfrac{2}{3}\mathrm{D}^2\big]f_3(\mathrm{Z}) - \big[\mathrm{D}^3 + 3(b_2{}^3-b_1{}^3) \\
& \quad - \tfrac{3}{2}(b_2\rho_2a_2{}^2 - b_1\rho_1a_1{}^2) - \tfrac{3}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}\big]f_9(\mathrm{Z})\big]r^{-5} \\
& + \big[-\tfrac{225}{32}\mathrm{Z}l^4f_5(\mathrm{Z}) - \tfrac{75}{8}\mathrm{X}l^3\mathrm{D}f_6(\mathrm{Z}) \\
& \quad + \tfrac{105}{8}\mathrm{Z}l^2\big[(b_2{}^2+b_1{}^2) - \tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2) + \tfrac{4}{7}\mathrm{D}^2\big]f_7(\mathrm{Z}) \\
& \quad + 15\mathrm{X}l\big[\mathrm{D}^3 + \tfrac{7}{2}(b_2{}^3-b_1{}^3) - \tfrac{9}{4}(b_2\rho_2a_2{}^2 - b_1\rho_1a_1{}^2) \\
& \quad - \tfrac{3}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}\big]f_8(\mathrm{Z}) - \tfrac{5}{4}\mathrm{Z}\big[\mathrm{D}^4 + 7(b_2{}^4+b_1{}^4) \\
& \quad + \tfrac{3}{4}(\rho_2a_2{}^2+\rho_1a_1{}^2)^2 + \tfrac{3}{8}(\rho_2a_2{}^4+\rho_1a_1{}^4) \\
& \quad - 3(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}^2 \\
& \quad - 9(b_2{}^2\rho_2a_2{}^2 + b_1{}^2\rho_1a_1{}^2)\big]f_{10}(\mathrm{Z})\big]r^{-6}\ldots\Big\}. \quad . \quad . \quad (98)
\end{aligned}
$$

And finally the force upon the whole atom, H_1, due to the second atom, H_2, is found by adding (81) without the r^{-2} term to (97) for the x-component, and adding (92) without its r^{-2} term to (98) for the z-component, giving (99) and (100), which follow.

$$
\begin{aligned}
\underset{\mathrm{H_2 on H_1}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\Big\{ & \big[-3(2-5\mathrm{Z}^2)\mathrm{X}l^2 + 6(4-5\mathrm{Z}^2)\mathrm{Z}l\mathrm{D} \\
& \quad + 3(1-5\mathrm{Z}^2)\mathrm{X}\mathrm{D}^2\big]r^{-4} \\
& + \big[\tfrac{3}{2}l^3f_0(\mathrm{Z}) - \tfrac{45}{2}l^2\mathrm{D}f_1(\mathrm{Z}) - 3l\big[(b_2{}^2+b_1{}^2) \\
& \quad - \tfrac{1}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2) + \mathrm{D}^2\big]f_2(\mathrm{Z}) + 5\big[\mathrm{D}^3 + 2(b_2{}^3-b_1{}^3) \\
& \quad - \tfrac{3}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}\big]f_3(\mathrm{Z})\big]r^{-5} \\
& + \big[-\tfrac{35}{2}\mathrm{X}l^4f_4(\mathrm{Z}) + \tfrac{105}{4}\mathrm{Z}l^3\mathrm{D}f_5(\mathrm{Z}) \\
& \quad + \tfrac{15}{2}\mathrm{X}l^2\big[\mathrm{D}^2 + \tfrac{3}{2}(b_2{}^2+b_1{}^2) - \tfrac{3}{4}(\rho_2a_2{}^2+\rho_1a_1{}^2)\big]f_6(\mathrm{Z}) \\
& \quad - 5\mathrm{Z}l\big[\mathrm{D}^3 + 3(b_2{}^3-b_1{}^3) - \tfrac{3}{2}(b_2\rho_2a_2{}^2 - b_1\rho_1a_1{}^2) \\
& \quad - \tfrac{3}{2}(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}\big]f_7(\mathrm{Z}) - \tfrac{15}{4}\mathrm{X}\big[\mathrm{D}^4 + 6(b_2{}^4+b_1{}^4) \\
& \quad + \tfrac{3}{4}(\rho_2a_2{}^2+\rho_1a_1{}^2)^2 - 3(\rho_2a_2{}^2+\rho_1a_1{}^2)\mathrm{D}^2 \\
& \quad - 6(b_2{}^2\rho_2a_2{}^2 + b_1{}^2\rho_1a_1{}^2)\big]f_8(\mathrm{Z})\big]r^{-6}\ldots\Big\}. \quad . \quad . \quad (99)
\end{aligned}
$$

$$
\begin{aligned}
\underset{H_2 \text{ on } H_1}{F_z} = \frac{e^2}{k}\Big\{ & \big[-3(4-5Z^2)Zl^3 \\
& -6(1-5Z^2)XlD+3(3-5Z^2)ZD^2\big]r^{-4} \\
& +\big[\tfrac{15}{2}l^3 f_1(Z)+\tfrac{9}{2}l^2 D f_2(Z)-15l[(b_2^2+b_1^2) \\
& \quad -\tfrac{1}{2}(\rho_2 a_2^2+\rho_1 a_1^2)+D^2]f_3(Z)-[D^3+2(b_2^3-b_1^3) \\
& \quad -\tfrac{3}{2}(\rho_2 a_2^2+\rho_1 a_1^2)D]f_9(Z)\big]r^{-5} \\
& +\big[-\tfrac{45}{2}Zl^4 f_5(Z)-\tfrac{35}{4}Xl^3 D f_6(Z) \\
& \quad +\tfrac{15}{4}Zl^2[D^2+2(b_2^2+b_1^2)-(\rho_2 a_2^2+\rho_1 a_1^2)]f_7(Z) \\
& \quad +15Xl[D^3+3(b_2^3-b_1^3)+\tfrac{3}{2}(b_2\rho_2 a_2^2-b_1\rho_1 a_1^2) \\
& \quad -\tfrac{3}{2}(\rho_2 a_2^2+\rho_1 a_1^2)D]f_8(Z)-\tfrac{5}{4}Z[D^4+6(b_2^4+b_1^4) \\
& \quad +\tfrac{3}{4}(\rho_2 a_2^2+\rho_1 a_1^2)^2-3(\rho_2 a_2^2+\rho_1 a_1^2)D^2 \\
& \quad -6(b_2^2\rho_2 a_2^2+b_1^2\rho_1 a_1^2)]f_{10}(Z)\big]r^{-6}\ldots\Big\}, \quad . \quad (100)
\end{aligned}
$$

where the functions of Z are given by (82) to (94).

These equations reduce immediately to those for the symmetrical fixed atoms of fig. 3, (70) and (71), if the four electrons are made alike by putting $b_2=b_1$, $\rho_2=\rho_1$, and $a_2=a_1$, and if the atoms are made symmetrical by making $l=0$. In doing this both the r^{-4} and the r^{-5} terms disappear, so that the series, which begins with the r^{-4} term for the strained atom, begins with the r^{-6} for the symmetrical atom.

In the expressions for the force of H_2 on C, (81) and (92) without their r^{-2} terms, the odd power terms in r^{-3} and r^{-5} are present, whereas they are absent from the corresponding expressions for the symmetrical atoms in (64) and (65).

Another striking point of difference between these and the simpler equations is that the direction cosines, X and Z, are no longer factors of the whole force as they formerly were. We may now proceed to simplify some of the expressions by giving attention to the numerical values of the quantities concerned.

XIII. *The Introduction of Numerical Values in the above Equations.*

In the first place it is clear that both quantities, l and $D=b_2-b_1$, must be far smaller than b, for b_2 must have very nearly the same value as b_1. It has already been shown in (78) and (80) that

$$h=(b_2+b_1)-2b=\cdot 4164\times 10^{-18}\ \text{cm.}, \quad . \quad (101)$$

so that when the sum of the radii is concerned it differs by only about $\cdot 4 \times 10^{-18}$ cm. from $2b$, which difference is negligible by comparison with b. The same statement also applies to the quantity $(\rho_2 a_2^2 + \rho_1 a_1^2)$, which is closely equal to $2\rho a^2$. Hence the quantity,

$$(b_2^2 + b_1^2) - \tfrac{1}{2}(\rho_2 a_2^2 + \rho_1 a_1^2),$$

which occurs in the equations may without sensible error be replaced by

$$2(b^2 - \tfrac{1}{2}\rho a^2) = 2\mathrm{P},$$

where P is given by (67) above.

The largest forces concerned are those internal forces producing a strain within the atom, of which (81) and (92) without their r^{-2} terms represent the force upon the positive charge alone due to the second atom. In the position of stable equilibrium this force on the positive charge is exactly counterbalanced by the opposite forces upon the two negative electrons. The largest terms of this force are the r^{-3} and r^{-4} terms, the higher powers becoming rapidly small. For example, the largest part of the r^{-5} term of (81) is of the order $l\mathrm{P}r^{-5}$ as compared with the largest part of the r^{-4} term $\mathrm{P}r^{-4}$, or numerically, taking r in round numbers as 10^{-8} cm., the r^{-5} and r^{-4} terms compare as $l \times 10^{14}$ to 10^{6}. But l is of necessity far less than b in order that the atom remains intact, and in fact comes out of the order of 10^{-18} cm. Hence the r^{-5} and all following terms of (81) and (92) are negligible, and may be omitted without sensible error. Making these simplifications reduces (81) to the following simpler form:

$$\underset{\mathrm{H_2\ on\ C}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\{-2[(2-3\mathrm{Z}^2)l - 3\mathrm{XZD}]r^{-3} \\ -6(1-5\mathrm{Z}^2)\mathrm{XP}r^{-4}\ldots\}, \quad . \quad (102)$$

and (92) to the following:

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\{-2[3\mathrm{XZ}l + (1-3\mathrm{Z}^2)\mathrm{D}]r^{-3} \\ -6(3-5\mathrm{Z}^2)\mathrm{ZP}r^{-4}\ldots\}, \quad . \quad (103)$$

The whole of the r^{-3} terms have been retained, but the r^{-4} terms have been simplified by omitting the l^2 and the $l\mathrm{D}$ parts because they are very small as compared with P.

XIV. *The Value of the Displacement "l."*

The x-component of the force of the second atom upon the positive charge, C, produces the strain in the atom represented by the small displacement, $l/2$, of figs. 4, 5, and 6. It is legitimate to take this displacement as proportional to the force producing it for very small displacements such as those contemplated. The force (102) may therefore be set equal to the displacement multiplied by some constant, say $\frac{e^2}{\mathrm{k}}\rho_x$, which is strictly characteristic of this form of atom. Since the displacement in one atom is $l/2$, we obtain

$$\underset{\mathrm{H_2\ on\ C}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\rho_x\frac{l}{2}. \quad . \quad . \quad . \quad . \quad . \quad (104)$$

The numerical value of this constant is unknown at present. A computation of its value might be made independently if we possessed the complete expression for the force of one oblate spheroid of charge acting upon another which is not yet known. It is evident that the approximate form for the electron used above, called the circle-and-point-electron, will not answer for such a purpose where the charges are so close as to be in contact with each other.

Upon equating (102) and (104) the $\frac{e^2}{\mathrm{k}}$ cancels, giving

$$-2(2-3\mathrm{Z}^2)lr^{-3}+6\mathrm{XZD}r^{-3}-6(1-5\mathrm{Z}^2)\mathrm{XP}r^{-4}=\rho_x\frac{l}{2}, \quad (105)$$

which may easily be solved for l, giving

$$l = \frac{3\mathrm{XZD}r^{-3}-3(1-5\mathrm{Z}^2)\mathrm{XP}r^{-4}}{(2-3\mathrm{Z}^2)r^{-3}+\rho_x/4}. \quad . \quad . \quad . \quad (106)$$

Similarly the z-component of the force upon C produces the strain within the atom which is represented by the small change in the semi-minor axes of the two electrons, the quantity $\mathrm{D}=b_2-b_1$ occurring in the equations. There is produced by it a change in the pressure between each electron and the positive charge. In the free state of the atoms b_2 and b_1 are equal to each other, their difference being zero; but as the molecule is formed, this difference changes gradually from zero to D, the forces upon the two electrons A and B being responsible for this change. For very small changes such as here contemplated it is legitimate to take D as proportional to the z-component of the force upon the positive charge, C, which is equal and opposite to the forces upon the two electrons in the position of equilibrium. Hence we may put

$$\underset{\mathrm{H_2\ on\ C}}{\mathrm{F}_z} = -\frac{e^2}{\mathrm{k}}\rho_z\mathrm{D}, \quad . \quad . \quad . \quad . \quad (107)$$

where ρ_z is some constant. That the negative sign is necessary here is apparent as follows:—If the z-component of the force upon C is positive, it acts in the upward direction in fig. 6, and must contract the upper electron A and expand the lower electron B. Hence b_2, which denotes the semi-minor axis for A, must be less than b_1, which denotes that of B. This would make b_2-b_1 negative when F_z is positive. The negative sign in (107) always makes F_z take the opposite sign to D, assuming that ρ_z is essentially positive, so that in the case just cited the force is positive. On the other hand, when F_z is negative and downward in fig. 6, then b_2 is greater than b_1 and D is positive, so that the negative sign is correct in either case.

Upon equating this new expression in (107) to (103), the $\frac{e^2}{\text{k}}$ cancels, giving

$$-6\text{X}\text{Z}lr^{-3}-2(1-3\text{Z}^2)\text{D}r^{-3}-6(3-5\text{Z}^2)\text{Z}\text{P}r^{-4}=-\rho_z\text{D}. \quad . \quad . \quad . \quad (108)$$

Solving for l gives a second independent value for this variable, which may be equated to that already obtained from the x-component in (106), and thus l is eliminated. We have

$$l=\frac{\rho_z/2-(1-3\text{Z}^2)r^{-3}}{3\text{X}\text{Z}r^{-3}}\text{D}-\frac{3-5\text{Z}^2}{\text{X}}\text{P}r^{-1}. \quad . \quad . \quad (109)$$

XVI. *The Value of* "D."

Upon equating (106) and (109) to eliminate l, we obtain the rather long expression,

$$\frac{9\text{X}^2\text{Z}^2r^{-6}-[(2-3\text{Z}^2)r^{-3}+\frac{1}{4}\rho_x][\frac{1}{2}\rho_z-(1-3\text{Z}^2)r^{-3}]}{3\text{X}\text{Z}r^{-3}[(2-3\text{Z}^2)r^{-3}+\frac{1}{4}\rho_x]}\text{D}$$
$$=\frac{3(1-5\text{Z}^2)\text{X}^2\text{P}r^{-4}-[(2-3\text{Z}^2)r^{-3}+\frac{1}{4}\rho_x](3-5\text{Z}^2)\text{P}r^{-1}}{\text{X}[(2-3\text{Z}^2)r^{-3}+\frac{1}{4}\rho_x]} \quad . \quad . \quad . \quad (110)$$

and by multiplying out the quantities in parentheses and reducing, the value of D obtained from this is

$$\text{D}=-3\text{Z}\text{P}r^{-4}\frac{(3-\text{Z}^2)r^{-3}+\frac{1}{4}(3-5\text{Z}^2)\rho_x}{2r^{-6}-[\frac{1}{2}(2-3\text{Z}^2)\rho_z-\frac{1}{4}(1-3\text{Z}^2)\rho_x]r^{-3}-\frac{1}{8}\rho_x\rho_z} \quad . \quad . \quad . \quad (111)$$

The expression for l in (106) involves the constant ρ_x, while that in (109) involves ρ_z; but the resulting expression for D involves both constants. To determine an equilibrium position for the two atoms does not depend so much upon the absolute values of the two constants as upon their relative values, and so far as can now be determined, their ratio may have any value. Let p denote this ratio, such that

$$\rho_z = p\rho_x. \qquad \qquad (112)$$

If an equilibrium is obtained when using certain assumed values of this ratio p, and if it is not obtainable when using quite different values of the ratio, it is legitimate to assume that the ratio that gives the equilibrium shall have the preference, and it is proper to search for such a value of the ratio as will give a definite position of equilibrium. It has been found that a ratio of $p=1/2$ gives a definite solution, but that with a ratio of $1/4$ there has been no success in finding an equilibrium position. This is quite different from stating that there is none, however; for the labour involved in a search for the equilibrium position after adopting some definite value for the ratio p is very great, so that the number of these ratios that has been tried is necessarily quite limited. We may content ourselves that a ratio has been found that produces any equilibrium at all. The reasons for this will appear when the process followed is given in more detail.

Therefore, adopting for the present the ratio $p=1/2$, the value of D in (111) reduces to

$$\mathrm{D} = -3\mathrm{ZP}r^{-4}\frac{(3-\mathrm{Z}^2)r^{-3}+\frac{1}{4}(3-5\mathrm{Z}^2)\rho_x}{2r^{-6}-\frac{1}{4}\rho_x r^{-3}-\frac{1}{16}\rho_x^2}. \qquad (113)$$

From this it is evident that D must pass through all values from $-\infty$ to $+\infty$ according to the relative positions of the two atoms. D is evidently zero when the numerator of (111) is zero. This is independent of the ratio p, whence for any value of this ratio we have $\mathrm{D}=0$ when

$$r^{-3} = -\tfrac{1}{4}\rho_x\frac{3-5\mathrm{Z}^2}{3-\mathrm{Z}^2}. \qquad (114)$$

This equation is plotted in polar coordinates in terms of Z and r in fig. 7, the curve marked "$\mathrm{D}=0$." When $\mathrm{Z}=1$ and the two atoms are in the coaxial position, then

$$r^{-3} = \tfrac{1}{4}\rho_x. \qquad (115)$$

And again, when the denominator of (113) is zero, then $\mathrm{D}=\infty$, and we have

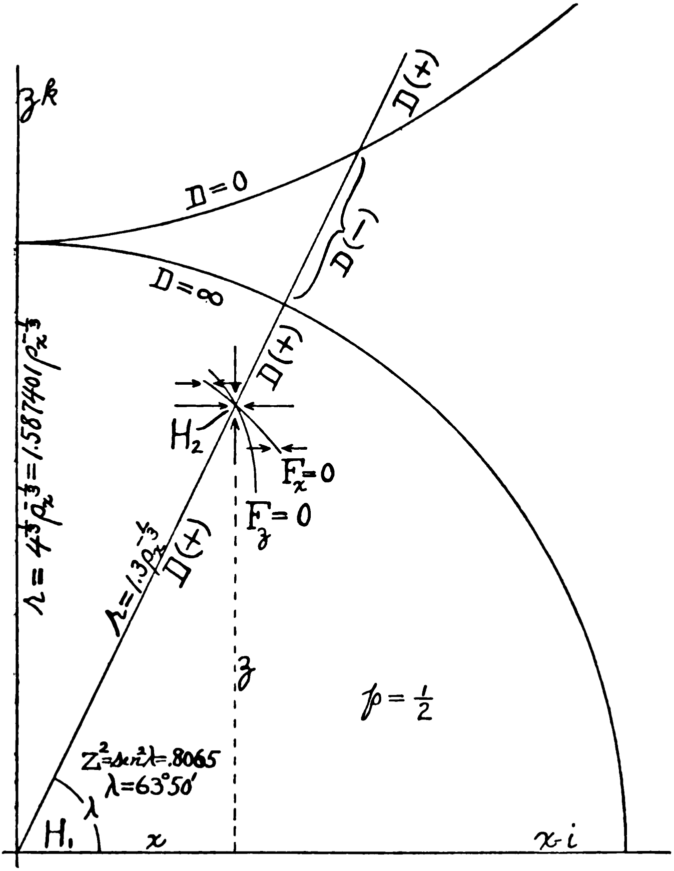
$$2r^{-6}-\tfrac{1}{4}\rho_x r^{-3} = \tfrac{1}{16}\rho_x^2, \qquad (116)$$

which is independent of the direction cosine, Z; and hence

D has the same infinite value at one fixed radius, r, for all angles or positions of the two atoms, r being the root of this equation. Solving, we find the two roots to be

$$r^{-3}=\tfrac{1}{4}\rho_x \quad \text{or} \quad -\tfrac{1}{8}\rho_x. \quad . \quad . \quad . \quad . \quad (117)$$

Fig. 7.



Illustrating the position of stable equilibrium for the two atoms of one hydrogen molecule.

The negative root has no physical significance, and the positive root is the same value as that above obtained in (115). The circle which this represents is shown in fig. 7 and marked "D=∞." The curves for D=0 and for D=∞ meet on the axis where Z=1. This is a critical point where both the numerator and the denominator of D in (113) have become zero. The value of D when Z=1 may be evaluated by putting Z=1 in that equation, giving

$$D=-3Pr^{-4}\frac{2r^{-3}-\frac{1}{2}\rho_x}{2r^{-6}-\frac{1}{4}\rho_x r^{-3}-\frac{1}{16}\rho_x^2}. \quad . \quad . \quad (118)$$

Now when $r^{-3}=\frac{\rho_x}{4}$ both the numerator and the denominator are zero, but the numerator is an exact factor of the denominator; and when this vanishing factor is cancelled, we have

$$D=-3Pr^{-4}\frac{1}{r^{-3}+\frac{1}{8}\rho_x}, \quad . \quad . \quad . \quad . \quad . \quad (119)$$

whence

$$D=\frac{2}{(4)^{1/3}}(-P\rho_x^{1/3})=1{\cdot}26(-P\rho_x^{1/3}) \quad . \quad . \quad (120)$$

It may be well to emphasize at this point that the meaning of the values of *l* and of D which are contemplated here is that, if the two atoms are placed in any given positions, the values of *l* and D must be those given by (109) and (113) for these positions, provided there exists any equilibrium for the two atoms at this point. An infinite value for *l* or D is manifestly impossible, so the interpretation is that there can be no equilibrium anywhere on the circle of radius

$$r=(4)^{1/3}\rho_x^{-1/3}=1{\cdot}587401\,\rho_x^{-1/3}, \quad . \quad . \quad . \quad (121)$$

because *l* and D never can be great enough to satisfy the conditions. The equilibrium position must lie elsewhere.

The value of D along any radius vector from the origin is negative between the circle where $D=\infty$ and the curve where $D=0$. It changes sign at these curves and becomes positive at distances greater than where $D=0$, and less than where $D=\infty$. The equilibrium position of the two atoms is evidently directly dependent upon the absolute values of the atomic constants, ρ_x and ρ_z, and the universal distance of 10^{-8} cm. between the two nearest atoms of a molecule is thus shown to depend in a very direct manner upon these atomic constants, and this in itself is sufficient reason for the existence of a universal distance. In finding the equilibrium position it is more convenient to reject or omit the constant multiplier throughout the work and then restore it again at the conclusion in the manner now to be described.

It has been shown that at one critical point r^{-3} depends directly upon ρ_x with a small multiplier, and that r depends upon $\rho_x^{-1/3}$. So we may say in general that

$$r=u\rho_x^{-1/3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (122)$$

where u may now be considered to represent the distance between the two atoms on a different scale if we choose.

And, similarly, we have shown that l and D each depend upon the quantity $(-\mathrm{P}\rho_x^{1/3})$ with a small multiplier, this being a positive quantity since P is negative. Hence we may write

$$l=l'(-\mathrm{P}\rho_x^{1/3}) \quad \text{and} \quad \mathrm{D}=\mathrm{D}'(-\mathrm{P}\rho_x^{1/3}), \quad . \quad . \quad (123)$$

and consider l' and D' as the small displacements in terms of a different unit. With these substitutions for r, l, and D in (106) we obtain

$$l'=\frac{3\mathrm{XZ}u^{-3}\mathrm{D}'+3(1-5\mathrm{Z}^2)\mathrm{X}u^{-4}}{(2-3\mathrm{Z}^2)u^{-3}+\frac{1}{4}}, \quad . \quad . \quad . \quad (124)$$

where the constant ρ_x does not appear. And, similarly (109) becomes

$$l'=\frac{\frac{1}{4}-(1-3\mathrm{Z}^2)u^{-3}}{3\mathrm{XZ}u^{-3}}\mathrm{D}'+\frac{3-5\mathrm{Z}^2}{\mathrm{X}}u^{-1}, \quad . \quad . \quad (125)$$

and (113) becomes

$$\mathrm{D}'=3\mathrm{Z}u^{-4}\frac{(3-\mathrm{Z}^2)u^{-3}+\frac{1}{4}(3-5\mathrm{Z}^2)}{2u^{-6}-\frac{1}{4}u^{-3}+\frac{1}{16}}. \quad . \quad . \quad (126)$$

XVI. *The Simplified Equations of the Force of the Second Atom upon the First.*

The final test of the equilibrium positions of the two atoms of the molecule must be that the complete equations for F_x and F_z, (99) and (100), are fully satisfied in addition to the two equations (125) and (126), these thus forming a set of four simultaneous equations containing but four variables, l', D', Z, and u.

When numerical values are introduced, many of the terms of (99) and (100) are seen to be quite negligible, and, in fact, they reduce to the following after substituting for l, D, and r their equivalents in (122) and (123):—

$$\begin{aligned}\underset{\mathrm{H}_2\,\mathrm{on}\,\mathrm{H}_1}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\{[&-3(2-5\mathrm{Z}^2)\mathrm{X}l'^2+6(4-5\mathrm{Z}^2)\mathrm{Z}l'\mathrm{D}' \\ &+3(1-5\mathrm{Z}^2)\mathrm{XD}'^2]u^{-4} \\ &+[6(4-35\mathrm{Z}^2+35\mathrm{Z}^4)l'-30(3-7\mathrm{Z}^2)\mathrm{XZD}']u^{-5} \\ &-45(1-14\mathrm{Z}^2+21\mathrm{Z}^4)\mathrm{X}u^{-6}\ldots\}\mathrm{P}^2\rho_x^2; \quad . \quad (127)\end{aligned}$$

$$\begin{aligned}\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\{[&-3(4-5\mathrm{Z}^2)\mathrm{Z}l'^2-6(1-5\mathrm{Z}^2)\mathrm{X}l'\mathrm{D}' \\ &+3(3-5\mathrm{Z}^2)\mathrm{ZD}'^2]u^{-4} \\ &+[30(3-7\mathrm{Z}^2)\mathrm{XZ}l'+6(3-30\mathrm{Z}^2+35\mathrm{Z}^4)\mathrm{D}']u^{-5} \\ &-15(15-70\mathrm{Z}^2+63\mathrm{Z}^4)\mathrm{Z}u^{-6}\ldots\}\mathrm{P}^2\rho_x^2. \quad . \quad (128)\end{aligned}$$

The whole of the r^{-4} terms has been retained, but the r^{-5} and r^{-6} terms have been much simplified without sacrificing any accuracy by omitting the l^3 and the l^2 D parts in the r^{-5} terms, since these are negligible as compared with Pl or PD, and in the r^{-6} terms all parts are omitted as negligible except the P^2 terms. The latter are the same electrostatic terms as given above in (70) and (71) for symmetrical atoms where l and D were supposed to be zero. If l' and D′ are each put equal to zero in (99) and (100), the whole force reduces to these important r^{-6} terms as formerly.

XVII. *The Process of Computation of the Equilibrium Position.*

The process of computation of the equilibrium position of the two atoms in the molecule may be outlined as follows. The immediate object is to find the locus of all points where the x-component of the force in (127) vanishes, plotting this as a curve. The locus of all points where the z-component vanishes is then plotted as a second curve. The total electrostatic force upon the first atom due to the second, or on the second due to the first, is then zero at all the points of intersection of these two curves, which give the equilibrium positions. Some of these intersections may correspond to unstable, and others to stable, positions; and since we are only interested in the stable positions each point must be examined to prove whether there is stability or not.

Since it requires a considerable amount of computation to obtain even a single point on either the $F_x=0$ or the $F_z=0$ curves, it is evident that the work is magnified many fold to trace these curves throughout the whole quadrant. This is our apology for not giving the curves complete throughout the quadrant, even for one single value of p, the ratio of the two constants ρ_z and ρ_x. Let us first assume a definite radius vector corresponding to some fixed value of Z, say such that $Z^2=0{\cdot}8$. Then (124) and (125) reduce to

$$l' = \frac{1{\cdot}2u^{-3}D' - 4{\cdot}02489u^{-4}}{-0{\cdot}4u^{-3}+0{\cdot}25}, \quad . \quad . \quad . \quad . \quad (129)$$

$$l' = \frac{0{\cdot}25+1{\cdot}4u^{-3}}{1{\cdot}2u^{-3}}D' = \frac{u^{-1}}{0{\cdot}44721}. \quad . \quad . \quad (130)$$

The expressions for the forces in (127) and (128) become

$$\underset{\substack{\mathrm{H_2\ on\ H_1}\\ \mathrm{Z^2=0\cdot8}}}{\mathrm{F}_x} = \frac{e_2}{\mathrm{k}}\{[2\cdot6833l'^2-4\cdot02489\mathrm{D}'^2]u^{-4} + [-9\cdot6l'+31\cdot2\mathrm{D}']u^{-5}-65\cdot2032u^{-6}\}\mathrm{P}^2\rho_x^2, \quad . \quad . \quad . \quad . \quad . \quad (131)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\{[8\cdot04978l'\mathrm{D}'-2\cdot6833\mathrm{D}'^2]u^{-4} + [-31\cdot2l'+8\cdot4\mathrm{D}']u^{-5}+9\cdot1232u^{-6}\}\mathrm{P}^2\rho_x^2. \quad . \quad . \quad . \quad . \quad . \quad (132)$$

Some arbitrary value of u may now be selected, say $u=1\cdot3$, and l' and D' computed by (129) and (130). The resulting numerical values are

$$l' = 3\cdot09 \quad \text{and} \quad \mathrm{D}' = 2\cdot961. \quad . \quad . \quad . \quad (133)$$

Using these numerical values, (131) and (132) become term by term

$$\underset{\substack{\mathrm{H_2\ on\ H_1}\\ \mathrm{Z^2=0\cdot8}\\ u=1\cdot3}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\Big\{\overset{r^{-4}\text{ term}}{-3\cdot392}\overset{r^{-5}\text{ term}}{+16\cdot81}\overset{r^{-6}\text{ term}}{-13\cdot52}\Big\}\mathrm{P}^2\rho_x^2 = \frac{e^2}{\mathrm{k}}(0\cdot102)\mathrm{P}^2\rho_x^2, \quad . \quad . \quad . \quad (134)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\Big\{17\cdot55 \ -19\cdot27+1\cdot982\Big\}\mathrm{P}^2\rho_x^2 = \frac{e^2}{\mathrm{k}}(0\cdot262)\mathrm{P}^2\rho_x^2. \quad . \quad . \quad . \quad (135)$$

According to this result each component of the force is very small as compared with the individual terms that are added, showing that the position selected is very near to the place where the forces vanish. Because the z-component of the force is positive, it indicates that the distance, u, should be reduced to make this component vanish, since this means an upward force on the first atom at the origin and a downward force on the second atom tending to reduce the distance. Trying another value of u less than 1·3, say $u=1\cdot29$, gives for l' and D' by (129) and (130),

$$l' = 3\cdot023 \quad \text{and} \quad \mathrm{D}' = 2\cdot946, \quad . \quad . \quad . \quad (136$$

whence by (131) and (132)

$$\underset{\substack{\mathrm{H_2\ on\ H_1}\\ \mathrm{Z=0\cdot8}\\ u=1\cdot29}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\Big\{\overset{r^{-4}\text{ term}}{-3\cdot758}\overset{r^{-5}\text{ term}}{+17\cdot625}\overset{r^{-6}\text{ term}}{-14\cdot15}\Big\}\mathrm{P}^2\rho_x^2 = \frac{e^2}{\mathrm{k}}(-0\cdot283)\mathrm{P}^2\rho_x^2, \quad . \quad . \quad . \quad (137)$$

$$\mathrm{F}_z = \frac{e^2}{\mathrm{k}}\Big\{17\cdot47-19\cdot52 \ +1\cdot982\Big\}\mathrm{P}^2\rho_x^2 = \frac{e^2}{\mathrm{k}}(-0\cdot068)\mathrm{P}^2\rho_x^2. \quad . \quad . \quad . \quad (138)$$

According to this result, both components of the force have changed sign somewhere between the values of $u=1{\cdot}3$ and $u=1{\cdot}29$, so that by interpolation we find approximately that

$$\left.\begin{aligned} &F_x = 0 \quad \text{when} \quad u = 1{\cdot}2972 \\ \text{and} \quad &F_z = 0 \quad \text{when} \quad u = 1{\cdot}2920 \end{aligned}\right\}. \quad . \quad . \quad (139)$$

Thus far, but a single point on each $F_x=0$ and $F_z=0$ curve has been found, and the value of Z in the general equations (124) to (128) may next be changed.

Taking $Z^2=0{\cdot}82$ instead of $0{\cdot}8$ gives

$$l' = \frac{1{\cdot}15256u^{-3}D' - 3{\cdot}9457u^{-4}}{-0{\cdot}46u^{-3}+0{\cdot}25}, \quad . \quad . \quad . \quad . \quad (140)$$

$$l' = \frac{0{\cdot}25 + 1{\cdot}46u^{-3}}{1{\cdot}15256u^{-3}}D' - 2{\cdot}593u^{-1}, \quad . \quad . \quad . \quad . \quad (141)$$

$$\underset{\substack{H_1 \text{ on } H_1 \\ Z^2=\cdot 82}}{F_x} = \frac{e^2}{k}\{[2{\cdot}6728l'^2 - 0{\cdot}54332l'D' - 3{\cdot}9456D'^2]u^{-4} + [-6{\cdot}996l' + 31{\cdot}58D']u^{-5} - 69{\cdot}5014u^{-6}\}P^2\rho_x{}^2, \quad . \quad . \quad . \quad (142)$$

$$F_z = \frac{e^2}{k}\{[0{\cdot}27166l'^2 + 7{\cdot}8912l'D' - 2{\cdot}9883D'^2]u^{-4} + [-31{\cdot}58l' + 11{\cdot}604D']u^{-5} + 0{\cdot}527u^{-6}\}P^2\rho_x{}^2. \quad . \quad . \quad . \quad (143)$$

When $u=1{\cdot}3$, we find from (140) and (141),

$$l' = 3{\cdot}023 \quad \text{and} \quad D' = 2{\cdot}878, \quad . \quad . \quad . \quad (144)$$

and from (142) and (143),

$$\underset{\substack{Z^2=0{\cdot}82 \\ u=1{\cdot}3}}{F_x} = \frac{e^2}{k}\left\{\overset{r^{\;-4}\text{term}}{-4{\cdot}56} \overset{r^{-5}\text{term}}{+18{\cdot}82} \overset{r^{-6}\text{term}}{-14{\cdot}41}\right\}P^2\rho_x{}^2 = \frac{e^2}{k}(-0{\cdot}15)P^2\rho_x{}^2, \quad . \quad . \quad (145)$$

$$F_z = \frac{e^2}{k}\left\{+16{\cdot}23 - 16{\cdot}74 + 0{\cdot}1093\right\}P^2\rho_x{}^2 = \frac{e^2}{k}(-0{\cdot}40)P^2\rho_x{}^2. \quad . \quad . \quad . \quad (146)$$

In order to show how the various terms vary it has seemed best to give these computations in some detail, and so, when u is increased from $1{\cdot}3$ to $1{\cdot}31$, we find instead of (144)

$$l' = 3{\cdot}077 \quad \text{and} \quad D' = 2{\cdot}883, \quad . \quad . \quad . \quad (147)$$

and instead of (145) and (146), we find

$$\underset{\substack{Z^2=0\cdot82\\u=1\cdot31}}{F_x}=\frac{e^2}{k}\{-4\cdot18+18\cdot03-13\cdot77\}P^2\rho_x^2=\frac{e^2}{k}(+0\cdot80)P^2\rho_x^2, \quad . \; . \; . \quad (148)$$

$$F_z=\frac{e^2}{k}\{+16\cdot21-16\cdot51-0\cdot1045\}P^2\rho_x^2=\frac{e^2}{k}(-0\cdot20)P^2\rho_x^2. \quad . \; . \; . \quad (149)$$

The x-component changes sign from $-$ to $+$ between these two values of u, and by interpolation we find that

$$\text{When } Z^2=0\cdot82, \quad F_x=0 \text{ at } u=1\cdot3065. \quad . \; . \quad (150)$$

The z-component is still negative, but smaller than when $u=1\cdot3$, and upon trying $u=1\cdot32$, we find

$$l'=3\cdot174 \quad \text{and} \quad D'=2\cdot910, \quad . \; . \; . \quad (151)$$

and that $F_z=\frac{e^2}{k}(0\cdot085)P^2\rho_x^2$, having changed sign between 1·31 and 1·32. By interpolation we have

$$\text{When } Z^2=0\cdot82, \quad F_z=0 \text{ at } u=1\cdot317. \quad . \; . \quad (152)$$

These results show that when $Z^2=0\cdot82$, the $F_z=0$ curve lies outside of the $F_x=0$ curve, whereas, when $Z^2=0\cdot8$, as first assumed above, the $F_x=0$ curve lies outside of the $F_z=0$ curve. Consequently the two curves intersect at some point between $Z^2=0\cdot8$ and $Z^2=0\cdot82$. By interpolation the probable intersection occurs at approximately

$$\left.\begin{aligned} Z^2&=0\cdot8065 \quad \text{and} \quad u=1\cdot30,\\ l'&=3\cdot066 \quad \text{and} \quad D'=2\cdot935.\end{aligned}\right\} \quad . \; . \quad (153)$$

These $F_x=0$ and $F_z=0$ curves are shown in fig. 7 computed between the values $Z^2=0\cdot7$ and $Z^2=0\cdot86$, showing the intersection at the point given by (153) approximately. This point represents one of stable equilibrium rather than unstable, and it may be regarded as one solution of the problem. The stability may be shown by examining the directions of the forces on either side of the curves of zero force. When the radius vector is greater than the value corresponding to the $F_x=0$ curve, the x-component of the force of H_2 on H_1 is positive and of H_1 on H_2 negative, as indicated by the horizontal arrows directed towards the curve in the figure. Also for radii smaller than those corresponding to the curve the force changes sign and the arrows are again directed towards the curve. Any displacement to the right or left of this curve sets up forces that tend to bring the atom back to the curve, showing stability for the x-component.

And similarly for the z-component of the force. All forces surrounding the point of equilibrium are thus directed towards this point thus showing stability. The atoms tend to return to this position for displacements in any direction.

XVIII. *Absolute Values.*

While no way has been found to obtain a numerical value for the constant ρ_x in an *a priori* manner, this is not true of the other constant ρ_z. The definition of this constant is contained in the assumption made in (107), which is repeated here, that the force upon C is proportional to D; namely,

$$\underset{\mathrm{H_2\ on\ C}}{\mathrm{F}_z} = -\frac{e^2}{\mathrm{k}}\rho_z \mathrm{D}, \quad . \quad . \quad . \quad . \quad . \quad (107)$$

so the constant may be said to denote this force when D is unity.

But in (25) it was shown that the work done by the electron A in forming the molecule is

$$-\frac{e^2}{\mathrm{k}}(30\cdot 7\times 10^{24})(b_2-b) = -6\cdot 964\times 10^{6}(b_2-b), \quad . \quad (154)$$

while the work done upon B during the same interval is

$$-\frac{e^2}{\mathrm{k}}(30\cdot 7\times 10^{24})(b_1-b). \quad . \quad . \quad . \quad . \quad (155)$$

The sum of these energies, the first being negative and the second positive, was given in (74) as representing the work done by A over and above that done upon B, which represents one-half of the total energy of dissociation of the molecule. On the other hand, the difference between these energies is

$$-\frac{e^2}{\mathrm{k}}(30\cdot 7\times 10^{24})\mathrm{D}. \quad . \quad . \quad . \quad . \quad . \quad (156)$$

Since each of the above energies is large as compared with their difference, the last expression is very approximately double the energy change for each electron, disregarding the sign. One-half of this, then, represents the energy given up by A and received by B. So the energy change to decrease the semi-minor axis of B by the amount a, or to increase that of A by the same amount (see (75) and (76), is

$$\frac{1}{2}\frac{e^2}{\mathrm{k}}(30{\cdot}7\times 10^{24})\,\mathrm{D}. \quad . \quad . \quad . \quad . \quad . \qquad (157)$$

But for a unit distance, or for D equal to unity, the energy and the force required to make this change in the energy are numerically equal to each other. The force is given by one-half of (107) above, since the force on the positive charge is the sum of that on the two electrons; whence it follows that the constant ρ_z is the numeric that occurs in (156), and we have

$$\rho_z = 30{\cdot}7\times 10^{24}. \quad . \quad . \quad . \quad . \quad . \qquad (158)$$

At the position of equilibrium found above we have

$$r = u\rho_x^{-1/3} = 1{\cdot}3\rho_z^{-1/3}, \text{ or } r^{-3} = 0{\cdot}455\rho_x \quad . \qquad (159)$$

and

$$\mathrm{D} = \mathrm{D}'(-\mathrm{P}\rho_x^{1/3}) = 2{\cdot}935(-\mathrm{P}\rho_x^{1/3}). \quad . \quad . \qquad (160)$$

If $\rho_z = \rho_x/2$, as was previously assumed in the special case in which the equilibrium was obtained, then

$$r^{-3} = 0{\cdot}91\rho_z = 0{\cdot}91\times 30{\cdot}7\times 10^{24} = 27{\cdot}94\times 10^{24}$$

and

$$r = 0{\cdot}3295\times 10^{-8} \text{ cm.} \quad . \quad . \quad . \quad . \qquad (161)$$

and

$$\begin{aligned}\mathrm{D} &= 2{\cdot}935\times 1{\cdot}25\times 10^{-26}\times 3{\cdot}945\times 10^{8}\\ &= 14{\cdot}47\times 10^{-18} \text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (162)\end{aligned}$$

and

$$\begin{aligned}l &= 3{\cdot}066\times 1{\cdot}25\times 10^{-26}\times 3{\cdot}945\times 10^{8}\\ &= 15{\cdot}11\times 10^{-18} \text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (163)\end{aligned}$$

According to this result, the order of magnitude of the distance between the atoms is 10^{-8} cm. in round numbers, which is in accord with the known facts emphasized at the beginning of this paper. The precise value cannot, of course, be obtained until the other constant, ρ_x, is computed in a direct manner from the electrostatic forces; but it is subject to computation, as before stated, on the basis of the atom model.

For example, if an equilibrium were obtained when the ratio p is made equal to unity and $\rho_z = \rho_x$, then the value of r would have been, instead of $\cdot 3295\times 10^{-8}$ cm., according to (159),

$$r = u(0{\cdot}322)10^{-8}; \quad . \quad . \quad . \quad . \quad . \qquad (164)$$

and if the equilibrium distance u came out $1{\cdot}5525$ instead of

1·3 as above, which is quite possible, then the distance r comes out

$$r = 0·5 \times 10^{-8} \text{ cm.}, \quad . \quad . \quad . \quad . \quad . \qquad (165)$$

which is the value that agrees with the experimental evidence as well as any other. The reason for not working out many cases of the equilibrium is just because we lack any *a priori* knowledge of the unknown constant ρ_r. But it is probable that it does not differ greatly from ρ_z, and by means of this the order of magnitude of the distance is established theoretically as depending directly upon the property of the electron.

Using the same value of the ratio, $p = 1/2$, as before, which is as good as another so far as we know, it is interesting to study the order of magnitude of the small displacements l and D. According to (77) and (162), we find

$$D = b_2 - b_1 = 2a + h = 14·47 \times 10^{-18} \text{ cm.}, \quad . \qquad (166)$$

and the value of h was found in (80) to be $0·4164 \times 10^{-18}$ cm. Hence

$$a = 7·027 \times 10^{-18} \text{ cm.}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (167)$$

which represents the total change in the semi-minor axis of electron B as the molecule is formed from free atoms. The expansion of the semi-axis of electron A is greater by the amount h, so that the new semi-axes, which were assumed as exactly 10^{-13} cm. in the free atom, become

$$\left.\begin{array}{ll} \text{for A} & b_2 = 1·000{,}074{,}43 \times 10^{-13} \text{ cm.}, \\ \text{and for B} & b_1 = 0·999{,}929{,}73 \times 10^{-13} \text{ cm.} \end{array}\right\} \quad . \quad . \qquad (168)$$

In making these changes the electron A gave up an amount of energy

$$\Delta E_A = -6·964 \times 10^6 (b_2 - b) = -51·83 \times 10^{-12} \text{ erg}, \quad . \qquad (169)$$

while the electron B absorbed an amount of energy

$$\Delta E_B = -6·964 \times 10^6 (b_1 - b) = +48·93 \times 10^{-12} \text{ erg}. \quad . \qquad (170)$$

The sum of this negative and positive energy represents the part of the original energy content of the two electrons that is used in forming the molecule, which is

$$\begin{aligned} \Delta E_A + \Delta E_B &= -6·964 \times 10^6 [(b_2 + b_1) - 2b] \\ &= -6·964 \times 10^6 h = -2·9 \times 10^{-12} \text{ erg}. \quad . \qquad (171) \end{aligned}$$

This is just half of the energy of dissociation of the molecule, namely $5·8 \times 10^{-12}$ erg as determined experimentally, and the same value is obtained by adding (169) and (170).

According to this, nearly seventeen times as much energy is passed across from the electron A to B as is used in forming the molecule—that is, in binding the second atom to the system. The actual change in the minor axis of either electron is minutely small as compared with the minor axis itself, the minor axis being about 14,200 times greater. It has been shown conclusively, however, that on the basis of the electrostatic forces alone this very small asymmetry of the two electrons is responsible for the formation of the molecule.

The displacement of the positive charge C off from the centre line of the two electrons represented by $l/2$ is given by (163) above. Bearing in mind that the semi-major axis of the positive charge (6) is $7{\cdot}054\times 10^{-16}$ cm., it appears that this displacement is only a small fraction of its own radius, about the ninety-third part of it. This fact is sufficient to show that it would be futile to attempt to derive the constant ρ_x by assuming that the positive charge may be regarded as a point charge, for only the minutest portion of the charge crosses the centre line joining the two electrons. The major portion of it still remains on either side after the displacement, and yet this very small displacement, together with the displacement D discussed above, is sufficient to account for the formation of the molecule.

XIX. *The Stress within the Atom.*

The force upon the positive charge C in the direction of the x-axis or equatorial direction is given by (104), which now becomes numerically

$$\underset{\mathrm{H_2\ on\ C}}{\mathrm{F}_x} = \frac{e^2}{\mathrm{k}}\rho_x\frac{l}{2} = \frac{e^2}{\mathrm{k}}464\times 10^6. \quad . \quad . \quad . \quad (172)$$

This is a comparatively large force, being the equivalent of the repulsion between two electrons at a distance of only about $4{\cdot}6\times 10^{-5}$ cm. from each other. On the other hand, for comparison the order of magnitude of the forces upon the whole atom near to their position of equilibrium by (127) and (128) is

$$\frac{e^2}{\mathrm{k}}\mathrm{P}^2\rho_x{}^2 = \frac{e^2}{\mathrm{k}}(590\times 10^{-3}), \quad . \quad . \quad . \quad (173)$$

which is nearly 10^9 times smaller than the forces producing the internal strain.

XX. *The Coaxial Position.*

It may be shown that there can be no equilibrium for the two atoms of the molecule when in the coaxial position, no matter what the relative values of the constants ρ_x and ρ_z may be. These constants are essentially positive, and their ratio, p, is also necessarily positive. Putting $Z=1$ and $X=0$ in (102) and equating to (104) gives

$$2lr^{-3}=\rho_x\frac{l}{2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (174)$$

from which l cancels, giving the same result as in (115) above, and which must hold true for any and every value of l. That is to say, l cannot be determined from (102). And again making $Z=1$ and $X=0$ in (127) and equating to zero gives

$$-6l'D'u^{-4}+24l'u^{-5}=0, \quad . \quad . \quad . \quad . \quad (175)$$

whence

$$D'=4u^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (176)$$

But when (103) is equated to (107) and $Z=1$, $X=0$, we have

$$4Dr^{-3}+12Pr^{-4}=-\rho_zD=-p\rho_xD. \quad . \quad . \quad (177)$$

Since r^{-3} must be $\frac{1}{4}\rho_x$ at the equilibrium position according to (174), it follows that

$$D'=\frac{3}{(4)^{1/3}}\frac{1}{1+p}=\frac{D}{(-P\rho_x^{1/3})}. \quad . \quad . \quad . \quad (178)$$

When $p=1/2$, as was assumed in the case previously discussed, then

$$D=\frac{2}{(4)^{1/3}}(-P\rho_x^{1/3}), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (179)$$

which is the same value as in (120) for this particular case. But the two values found for D' in (176) and (178) must agree, so that

$$D'=4u^{-1}=4\frac{r^{-1}}{\rho_x^{1/3}}=\frac{4}{(4)^{1/3}}=\frac{3}{(4)^{1/3}}\cdot\frac{1}{1+p}, \quad . \quad (180)$$

whence $p=-1/4$, which is impossible, as before stated, because of the negative sign. Hence there exist no values of the constants ρ_x and ρ_z that will produce an equilibrium when the atoms have the coaxial position.

XXI. *Available and Unavailable Energy.*

There has been a renewed discussion recently of the old topic of releasing interatomic energy to be used for practical commercial purposes, some inclining to the view that the energy is so securely locked within the atoms that it will never be possible to release it, and others claiming that they have already attained the proof experimentally that the long-sought goal is within the realm of possibility. It seems worth while to examine this question once more in the light of the points that have been made in this paper. Both opinions seem likely to be substantiated, paradoxical as this may be. The total energy content of any mass of matter is expressed by mc^2, where m is its mass and c the velocity of light. By far the greater part of this is the energy content of the elementary bodies, the positive and negative charges, in their free states. This is not simply interatomic energy, but it is interelectronic energy as well.

In this paper it has been pointed out that in forming atoms and molecules out of these free elementary bodies some of their original energy content has been used, but that it is an extremely minute portion of the whole. Until we are prepared to admit, therefore, that a much larger part or even the whole energy content of the electrons may be abstracted, then it must remain true that this energy is so securely locked within the atoms that we may never expect to make it available energy for practical purposes. In this sense the first opinion above given is likely to be true.

On the other hand, even that minute portion of the energy content of the electrons, the portion actually given up in forming atoms, may be so much greater than the still smaller energies now available—let us say the energies of combustion, coal energy or chemical energy which is obtainable from an exchange of atoms in molecular structures—even that minute portion may be so much greater than the chemical energy now available that there is much assurance of the possibility of increasing the energy available at present many times. In this sense the second opinion above mentioned is likely to be substantiated, and both opinions may be correct, it depending entirely upon the value of interatomic energy that each had in mind in making the statements.

For example, we may think of 10^{-12} erg as the order of magnitude of the energies available at present derived from altering molecular structures in combustion, etc.—that is, the energy per molecule. This may be compared with the energy of single ionization of the hydrogen atom, about 35×10^{-12} erg, or with the energy of double ionization, which is not known exactly, but is many times greater than the single ionization energy. It seems quite probable that the energy required to separate the elementary fundamental bodies or charges within an atom itself, or to change them about just as is now done with the atoms in molecules, may sometime be used for practical purposes. At any rate, it may be looked upon as available energy in contradistinction to that locked within the electrons which is not available. This available energy may easily be more than 100×10^{-12} erg per atom, or more than 100 times the energy at present made use of, but it probably will never approach 100,000 times as much, at least until an electron may be made to give up all of its energy.

XXII. *Conclusion.*

The question foremost in the minds of all in examining a presentation of any new subject is: What has been accomplished of any practical value? This often reveals an impatience that there are not more practical results immediately in sight or to follow without much delay. If this investigation reveals anything, it is that it requires a considerable amount of patience and perseverance against odds to accomplish anything of value in this most intricate and involved subject. The form of atomic model considered in this paper has been so fruitful in enabling us to arrive at an understanding of so many phenomena that it must commend itself very forcefully to investigators. To have shown that electrostatic forces are quite sufficient to produce the formation of molecules, after the directions of the axes of rotation are taken care of by the electromagnetic forces due to the rotation of the elementary bodies, and that the order of magnitude of the distance between centres of nearest atoms must be of the order of 10^{-8} cm., as it is known to be in fact, is considered to be an important result that may hereafter have practical consequences.

It must be true, however, that we do not know much about even the simplest atoms until it is possible to answer such questions as the following for example:—Why is it that 44,000 small calories of energy are given up as heat per gram-molecule when hydrogen gas and chlorine unite to form HCl? But when nitrogen and oxygen are united together to form nitric oxide (NO) there occurs an absorption of 43,150 small calories of energy per gram-molecule instead of an evolution of energy as heat? Until we have a clear understanding of these phenomena in terms of some atomic model, it cannot be said that we know much about the atoms of nitrogen, oxygen, and chlorine. And so on through a whole list of elements these energy relations are of the greatest importance; but we are not aware of any other form of atomic model that throws any definite light on these questions. By means of the models discussed in this and previous papers, however, there is encouragement to think that some of these questions may receive a very definite answer.

This paper has dealt almost exclusively with the atom of hydrogen, because it is so very much simpler than all others; but it may readily be seen that the same principles apply to other atoms with equal force, although the computations become more complex. Nor has the investigation of hydrogen been completed; we still require the atomic constant ρ_r, which may be computed sometime. Then, too, more of the equilibrium curves similar to those of fig. 7 should be computed, for it is suspected that for some values of the constants there may be more than a single point that shows stability for the two atoms of the molecule. One may even suspect that there are two different equilibrium positions for the atoms in the hydrogen molecule from the behaviour of hydrogen itself. Hydrogen sometimes forms a molecule with three instead of two atoms according to Sir J. J. Thomson's discovery, and this is comparatively unstable. The difference between what is called "nascent hydrogen" and hydrogen may also be connected with these two possible stabilities suspected. The nascent form of hydrogen may be the more unstable form of molecule. This is now, of course, a matter of pure speculation, but it is just such unknown phenomena that supply the incentive to investigation.

Since the equilibrium as between the two atoms of a molecule is dependent upon a balance between the r^{-4}, r^{-5}, and r^{-6} terms of the force series, it should result from experiments in the compression and expansion of solids that the apparent law of force between atoms obeys some power intermediate between -4 and -6, probably the inverse fifth power approximately. This result is in close agreement with the experimental evidence as far as it is known.

And finally it is considered an important result to have shown that there exist constants characteristic of each atom, which are responsible for the universal distance of the order of 10^{-8} cm. between nearest atoms, as well as to have arrived at some understanding of their physical meaning, which reveals the necessity for their existence.

APPENDIX A.—*The Value of* $P = b^2 - \frac{1}{2}\rho a^2$.

For the purpose of approximation to the oblate spheroid by the substitution of the circle-and-point-electron in its stead, it is assumed that the ring is best represented by a circle whose radius is equal to the radius of gyration of the ring. By the ring is meant the part of the spheroid that remains after cutting out an inscribed sphere. The first requirement is then to find the radius of gyration of the ring.

The moment of inertia of the oblate spheroid about its minor axis is, assuming a uniform density throughout its volume,

$$I_{\text{O.S.}} = (\tfrac{4}{3}\pi a_0^2 bd)(\cdot 4a_0^2), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the first factor being the mass, and the second the square of the radius of gyration of the spheroid.

The moment of inertia of the inscribed sphere is

$$I_{\text{S}} = (\tfrac{4}{3}\pi b^3 d)(\cdot 4b^2). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The moment of inertia of the ring excluding the inscribed sphere is the difference between (1) and (2), namely

$$I_{\text{R}} = I_{\text{O.S}} - I_{\text{S}} = \tfrac{4}{3}\pi bd(a_0^2 - b^2)a^2 = \tfrac{4}{3}\pi bd(a_0^4 - b^4)(\cdot 4), \quad (3)$$

where a is the radius of gyration of the ring. Hence

$$a^2 = \cdot 4(a_0^2 + b^2), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where a is also the radius to be found, and which is used in the circle-and-point-electron.

According to (24) the eccentricity of the electron in the atom is $\epsilon = 0{\cdot}9547$, or

$$1 - \epsilon^2 = 1 - 0{\cdot}91145 = 0{\cdot}08855 \ ; \quad . \quad . \quad . \quad (5)$$

whence by (12)

$$a_0^2 = \frac{b^2}{1-\epsilon^2} = \frac{10^{-26}}{\cdot 08855} = 11{\cdot}3 \times 10^{-26} \quad . \quad . \quad . \quad (6)$$

$$\text{and} \qquad a^2 = \cdot 4(11{\cdot}3 + 1)10^{-26} = 4{\cdot}92 \times 10^{-26}, \quad . \quad . \quad (7)$$

$$\text{or} \qquad a = 2{\cdot}218 \times 10^{-13} \quad \text{and} \quad a_0 = 3{\cdot}36 \times 10^{-13} \text{ cm.} \quad . \quad (8)$$

Since by (45) above $\rho = \epsilon^2$, we find that

$$\rho a^2 = 0{\cdot}91145 \times 4{\cdot}92 \times 10^{-26} = 4{\cdot}484 \times 10^{-26}. \quad . \quad (9)$$

And hence

$$P = b^2 - \tfrac{1}{2}\rho a^2 = (1 - 2{\cdot}242)10^{-26} = -1{\cdot}242 \times 10^{-26}, \quad (10)$$

which was to be found. The value used in the paper is the even figure $-1{\cdot}25 \times 10^{-26}$.

LXXXIX. *An attempted Electrolytic Separation of the Isotopes of Chlorine and Magnesium.* *By* JOHN E. G. PILLEY *.

1. AT the Royal Society discussion on Isotopes (Proc. Roy. Soc. 1921) it was suggested by Professor Lindemann that it might be possible to separate isotopic ions by an electrolytic method depending on an expected difference between their migration velocities in solution. If such a difference existed, and if the fastest-moving ions could be isolated, it would be possible to obtain complete separation by this means.

The method depends upon the assumption that the ions are not large compared with the solvent molecules. For unless this were so, their velocity would be uniform and independent of the mass of the ion.

If the ions are of the same order of magnitude as the solvent molecules, the medium in which they move can scarcely be regarded as homogeneous. Although the resultant force of the surrounding molecules will vary between considerable limits, one might reasonably expect that one would obtain a first approximation of their behaviour by treating them as having a free path between collisions with solvent molecules. Hence the migration velocity of the ion, when measured over distances large compared with the molecular distances, could be treated as though it were made up of a large number of free paths over which there was a component of acceleration due to the electric force. Presumably the actual lengths of the free paths of isotopes are identical; and as their masses and velocities and therefore the times spent on such free paths are different, the migration velocities measured over large distances should also be different.

On this basis it is possible to obtain an estimate of the difference of mobility that could be expected.

Let m be the mass of the solvent molecules.

Let M be the mass of the ions.

Let V_m be the observed migration velocity.

Let V_0 be the average velocity due to the field after collision.

Let V_f be the average velocity due to the field before collision.

Let F be potential gradient.

Let E be the charge on the ion.

Let t be the time spent on a free path.

If, as assumed above, the greater part of the ion's change of momentum takes place in the neighbourhood of the solvent molecule, the problem reduces itself to that of an ion moving along a number of free paths terminated by collisions. If we adopt the view that the probability of an ion assuming any direction of motion after collision is equally great, but that the momentum along the axis of motion remains unaltered through collision, we obtain an expression relating the velocities before and after collision. If, as a first approximation, we treat the colliding particles as smooth spheres, then

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* Communicated by the Author.

$$\frac{V_0}{V_f} = \frac{M + \frac{(1-\epsilon)}{2} m}{M + m}, \quad \ldots \quad \text{(i.)}$$

where ϵ is the coefficient of restitution.

If t is the time interval between successive collisions, the electric field applied to the ion will produce a change of velocity such that

$$V_f = V_0 + \frac{FEt}{M}. \quad \ldots \quad \text{(ii.)}$$

Combining these two equations, we find that

$$V_0 = FEt\left(\frac{M + m\left(\frac{1-\epsilon}{2}\right)}{Mm\left(\frac{1+\epsilon}{2}\right)}\right). \quad \ldots \quad \text{(iii.)}$$

As the acceleration due to the field is uniform, the mean velocity of motion of the ion would be

$$V_a = V_0 + \frac{FEt}{2M}. \quad \ldots \quad \text{(iv.)}$$

Hence, substituting the value of V_0 from (iii.),

$$V_a = FEt\left(\frac{M + m\left(\frac{1-\epsilon}{2}\right)}{\left(\frac{1+\epsilon}{2}\right)Mm} + \frac{1}{2M}\right) = FEt\left(\frac{2M + \left(\frac{3-\epsilon}{2}\right)m}{(1+\epsilon)Mm}\right). \quad \ldots \quad \text{(v.)}$$

If r is the mean relative velocity of ion and solvent molecule, then the time occupied on a free path l will be such that

$$t = \frac{l}{r}.$$

The mean relative velocity is related to the mean velocities of the two colliding particles according to the well known formula of the kinetic theory:

$$r=\frac{3v_1^2+v_2^2}{3v_1},$$

where v_1 is the velocity of the faster-moving particle.

Considering the case where the mass of the ion is greater than that of the solvent molecule ($M>m$), and where consequently the ion has a smaller average velocity than the solvent molecule, then

$$V_1=\sqrt{\frac{3KT}{m}},$$

$$V_2=\sqrt{\frac{3KT}{M}}.$$

Since $$t=\frac{l}{r}=\frac{3lv_1}{3v_1^2+v_2^2}=\frac{3lM\sqrt{m}}{\sqrt{3KT}(3M+m)},$$

the migration velocity in terms of M and m becomes

$$V_a=FE\left[\frac{2M+\frac{3-\epsilon}{2}m}{(1+\epsilon)Mm}\times\frac{3lM\sqrt{m}}{\sqrt{3KT}(3M+m)}\right]$$

$$=\frac{3FEl}{(1-\epsilon)\sqrt{KTm}}\left[\frac{2M+\frac{3-\epsilon}{2}m}{3M+m}\right].$$

The percentage difference in mobility for unit difference of atomic weight M is therefore

$$\frac{1}{V_a}\frac{dV_a}{dM}=\frac{3}{3M+m}-\frac{2}{2M+\left(\frac{3-\epsilon}{2}\right)m}.$$

The result is slightly different in the case ($M<m$); that is to say, when the solvent molecule has the smaller velocity. In this case

$$V_a=FE\left[\frac{2M+\left(\frac{3-\epsilon}{2}\right)m}{(1+\epsilon)Mm}\times\frac{3lm\sqrt{M}}{\sqrt{3KT}(Mt+3m)}\right]$$

$$=\frac{3FEl}{(1+\epsilon)\sqrt{3KT}}\times\frac{2M+\left(\frac{3-\epsilon}{2}\right)m}{\sqrt{M}(M+3m)},$$

and consequently

$$\frac{1}{V_a}\frac{dV_a}{dM} = \frac{\frac{3}{2}\sqrt{M} + \frac{3m}{\sqrt{M}}}{\sqrt{M}(M+3m)} - \frac{2}{2M + \left(\frac{3-\epsilon}{2}\right)m}.$$

By substituting actual values of M and m in these equations, an estimate of the separation to be expected can be obtained.

Thus, for instance, in the case of chlorine ions, assuming that there is neither hydration of the ions nor association of the water molecules, namely that $M_1 = 35$, $M_2 = 37$, and $m = 18$, one finds

when $\epsilon = 1$ a difference of ·3 per cent.,
when $\epsilon = 0$ a difference of ·7 per cent.

between the calculated mobilities of the two isotopic ions. If, however, the water is polymerized and consists chiefly of $2(H_2O)$ molecules, a difference of about ·5 per cent. would be expected when $\epsilon = 1$, and 1·0 per cent. when $\epsilon = 0$.

If, lastly, the ions are hydrated and the solvent molecules associated, *e. g.* the ions have masses $(35+36)$ and $(37+36)$ respectively and the solvent molecules are of effective mass 36, one would still expect a difference of ·2 per cent. for $\epsilon = 1$ and ·4 per cent. for $\epsilon = 0$.

Even if the least favourable of these results were valid, a separation should be realizable.

2. *Experimental.*

In order to test whether isotopic mixtures could be resolved on this principle, two series of experiments were carried out: one with chlorine and the other with magnesium.

The method adopted was to allow the ions to move into an electrolyte, initially free from such ions, suspended in a jelly of agar-agar in order to reduce convectional mixing. After a suitable time the jelly was removed and the front boundary reached by the ions was cut off. The atomic weight of the element concerned as represented by these ions was then compared with that of the same element as represented by ions from the middle of the column.

The difference of mobility should be of the order of ·4 per cent. for a difference of two units in atomic weight. If a smaller fraction than this of the total number of ions transported is cut off from the head of the column, one would therefore expect to find a marked difference between their atomic weight and that of the rest of the ions. The scale of the experiments depends on the amount of the material desired; but the "cut" must be such that it is electro-chemically equivalent to less than ·2 per cent. or to ·3 per cent. of the whole time-current product.

A number of tubes 100 cm. long and 1·5 cm. diameter were filled, in the first series of experiments, with a half-normal potassium nitrate solution containing 30 grams of agar-agar per litre. The ends of the tubes fitted into the sides of specially constructed rectangular boxes which formed the anode and cathode compartments, and between which a potential difference of up to 300 volts could be maintained. The solution in the anode cell was prevented from becoming acid with half-normal potash, and similarly that in the cathode department was prevented from becoming alkaline with half-normal hydrochloric acid. The levels of the liquids in the two compartments were kept the same by means of a long, narrow gauge siphon. The tubes which lay horizontally between the two boxes were kept cool with a current of cold water, and thus the temperature of the electrolyte was prevented from rising unduly. As, however, both mobility and thermal diffusion are proportional to the square root of the absolute temperature, the effect of change in temperature is not serious.

In the earlier experiments, when the boundary had almost reached the anode end of the tube, electrolysis was stopped and the jelly pushed back so that the Cl/NO_3 boundary was at the cathode end again, and that the chlorine boundary might traverse a further length of nitrate solution.

The electrolysis was carried out for about fourteen hours with a voltage gradient of 3 volt/cm.

At the end of the experiment the position of the chlorine boundary was located by placing the jelly in an acid silver solution and observing the cloud of silver chloride formed.

As the absolute velocity of NO_3 ions is less than that of Cl ions, the front of the advancing Cl band was diffuse; and in order to estimate the amount being cut off, several successive "cuts" were made from each tube and the corresponding cuts from each identified by matching the intensities of the silver chloride clouds formed. The amount each cut contained was estimated subsequently.

A subsidiary series of experiments was carried out with potassium hydroxide instead of potassium nitrate in the tubes, and in these, since the OH ion has a much greater velocity than the Cl ion, a sharp boundary between the OH and Cl ions was produced.

The "front section" chlorine "cuts" from these two experiments were added and the atomic weight determined.

As each cut of the leading section was made, an equivalent amount was taken from half-way down the tube, and this provided material for a check atomic weight.

Chlorine was precipitated from both "front" and "middle" specimens as silver chloride, and this when thoroughly washed and dried was reduced in a stream of pure dry hydrogen prepared by the electrolysis of baryta water. The hydrochloric acid evolved was collected in pure conductivity water; and it was from these solutions that the pure silver chloride for atomic weight determinations was precipitated by the addition of just less than the amount of silver nitrate necessary for complete precipitation of the chlorine. The ratio AgCl : Ag was then determined by reducing this silver chloride after it had been carefully washed and dried.

For this reduction a double furnace was used which contained two tubes of pyrex glass side by side, into which small light silica boats containing the two samples of silver chloride to be compared could be placed. The tubes were enclosed in a nickel case in which they were heated by the same electric heater. The temperature was read with a thermo-junction in a thin glass tube just over the surface of each of the boats containing silver chloride. The precipitation and washing processes were conducted in a safe orange light, and nearly equal weights of the two kinds were placed in silica boats, also of almost the same weight. The chloride was finally dried in the dark in a stream of dry air. When the two specimens became constant in weight, the chloride was reduced in a stream of pure hydrogen and the silver formed carefully weighed.

Weighings were carried out on a sensitive assay balance, with the usual precautions for great accuracy. Not only were the weights of the two boats containing the samples compared, but the absolute weight of each was measured. The amounts used were small enough to render the correction for buoyancy almost negligible.

In four preliminary experiments with silver chloride prepared from pure silver nitrate it was found possible to obtain values of the atomic weight differing by less than ·1 per cent. of the accepted value of 35·46. Chlorine was re-precipitated as silver chloride from the hydrochloric acid collected from the reduction, and used for a further determination of atomic weight.

The values obtained for successive atomic weight determinations were :—

Front section.	Middle.
35·49	35·45
35·44	35·48
35·48	35·41

These results seemed definitely to indicate that no separation of the isotopic chlorine ions, of the order expected, had been effected. Since it seemed possible that there might be a specific action between the chlorine and the jelly, it was decided to make a second series of experiments with magnesium ions.

The difference of mobility to be expected is of the same order as with chlorine.

If $Mg = 24$,
$H_2O = 18$, the difference of mobility should be ·6 per cent. $(\epsilon = 1)$.

If $MgH_2O = 42$,
$2H_2O = 36$, the difference of mobility should be ·4 per cent. $(\epsilon = 1)$.

The experiment was made under almost the same conditions as in the case of chlorine. Tubes of the same dimensions were used, and filled with a jelly containing half-normal solution of ammonium sulphate. The anode compartment was filled with magnesium sulphate in which was suspended a large excess of magnesium oxide.

The position of the magnesium boundary in the tube at the end of the experiment was found by treating the jelly with an alkaline solution of ammonium oxalate. The fraction cut off was, as with chlorine, about 2 per cent. of the total amount transported by the current. At the same time, sections containing approximately the same weight of magnesium were cut off from the middle of the column of jelly impregnated with magnesium, to provide material for a check atomic weight.

The specimens of magnesium obtained from these two sources were purified alongside each other by identical chemical processes, and their atomic weights determined simultaneously. The first step in the purification was to calcine the jelly and to dissolve the residue in dilute sulphuric acid. The solution was next filtered and evaporated to drive off any excess of sulphuric acid.

The solution was then treated with ammonia and ammonium sulphide, and allowed to stand several hours in contact with the precipitant.

Calcium was next removed as oxalate from the filtrate by the method described by Blasdale, and the magnesium precipitated as phosphate with ammonia and sodium phosphate.

After thorough washing of the phosphate, the magnesium was obtained, in soluble form, by fusing with purest sodium carbonate. The washed carbonate was next dissolved in sulphuric acid. Traces of sodium remaining were removed by repeated precipitation of the magnesium as carbonate with an alcoholic solution of ammonia and ammonium carbonate and by thorough washing.

The magnesium carbonate was converted to sulphate, and finally purified by fractionation from a mixture of re-distilled alcohol and water.

The ammonia and ammonium sulphide were made by saturation of conductivity water with ammonia and sulphuretted hydrogen gases.

Pyrex vessels were used in the earlier part of the purification and platinum in the final processes.

The atomic weight of the magnesium in the two samples of magnesium sulphate purified in the above manner was then determined by converting to oxide according to a method used by Mr. A. C. Egerton in this laboratory. The accuracy of the determinations by many investigators of the ratio $MgSO_4 : MgO$ had been vitiated by occlusion of gas by the oxide obtained by ignition of the anhydrous sulphate. In order to overcome this difficulty, both the sulphate and the oxide were weighed in a high vacuum. For this purpose special light weighing bottles of Pyrex glass were constructed. The lids of the bottles carried small taps through which the bottles could be exhausted while the small platinum crucibles containing the sulphate or oxide were still hot. Both the lids and the taps were greased with special tap grease, and the bottles held a hard vacuum without leak. The total weight of the bottles with their crucibles was about twelve grams.

Approximately equal weights of the two samples of magnesium sulphate were weighed into two platinum crucibles, which were heated side by side in an electric resistance furnace to 600° until, after transferring to the weighing bottle, the weight became constant. The dry sulphate was next converted into oxide by heating the crucibles again side by side to 1150–1200° in an alundum muffle for several hours, the temperature being measured with an optical pyrometer and the oxide being weighed as described.

In a preliminary series of six determinations on some specially purified magnesium sulphate, Mr. Egerton has obtained agreement by this method in each case within ·03 units of the accepted value 24·32. The method was therefore deemed sufficiently accurate for the present purpose (where differences of about $\frac{1}{2}$ per cent. were being looked for), although the quantities available for the determinations were somewhat less than those used by Mr. Egerton.

In the first determinations the quantities of material (200 milligrams) were found to be insufficient to give reliable results, and further electrolyses were made; and after adding the first samples, the whole was re-purified and the atomic weights re-determined. The values obtained were :—

Front section.	Back section.
24·36	24·28
24·12	24·10
24·34	24·30

The values obtained for the atomic weight are affected by the conditions under which the magnesium sulphate is heated. The values in the second determination are, for example, both too low. As, however, the two specimens of magnesium compound were always subjected to the same treatment, the correspondence of the two values bears a greater significance than the actual values themselves.

The values for the back section are in every case slightly lower than those of the front section. The difference is, however, very small, and can scarcely be attributed to a separation.

The conclusion from these experiments seems to be that no separation, at least of the order expected, has occurred. It seems difficult to explain the failure of this method. There is very little doubt that the method would work if it could be applied to a gaseous system, and one must presumably therefore look for an explanation of its failure in the conditions characteristic of the liquid state.

In the first place the expression

$$V_f = V_0 + \frac{FEt}{M}$$

probably does not, at all accurately, express the motion of the ion between the events that we call collisions, as it presupposes a gradient of the field of force in the proximity of solvent molecules and ions very much greater than can reasonably be assumed. How great a difference a change in this assumption would introduce in the final result it is difficult to say, but it is possible that it might reduce the difference between the calculated mobilities considerably.

Furthermore, the expression

$$V_0 = V_f\left(\frac{M + m\left(\frac{1-\epsilon}{2}\right)}{M+m}\right)$$

may be considerably in error in representing the fraction of the initial velocity that remains after impact, as it involves the possibly false assumption that the velocities of molecules and ions, due to thermal agitation, can be assumed to cancel out, and that the velocities due to the electric field can be considered alone.

Neither of the above considerations could, however, lead to the conclusion that separation was impossible; for however small a fraction of the velocity before collision persists after it, accelerations (differing with the masses of the ions) must occur, and however short the path and time over which these accelerations take place, the average velocities of the two ions should never be quite the same.

If, on the other hand, there are factors which lead to variations of the velocities of individual ions independently of their masses, then separation might become indefinitely small.

There are several ways in which it may be suggested this variation could take place.

Firstly, the velocity might be reduced to zero through the ion becoming neutralized by combination with an ion of the opposite sign. In the case of $MgSO_4$ at half-normal concentration only 63·9 per cent. of the magnesium exists as ions, and in the case of half-normal KCl only 89·7 per cent. Thus, especially with magnesium, there would be a tendency for the faster ion to come to rest and to be overtaken by the slower one.

The same action would also take place if the jelly used in the experiments were capable of absorbing the ions. If this happened, the faster-moving ions would again be brought to rest and the slower catch them up.

If, lastly, the state of hydration (and consequently the mobilities) of the ions were to vary independently, a similar result would ensue. If there were a dynamic equilibrium of the kind,

$$Cl' + nH_2O \rightleftharpoons Cl'H_2O + (n-1)H_2O \rightleftharpoons Cl'2H_2O + (n-2)H_2O,$$

the mobility of the ion could have several distinct values.

The effect following from any of these three causes would be such as to make it useless to increase the distance, over which separation was attempted, above the average length individual ions could move without being affected by any of them. As this average distance would be small, it would be impossible to achieve any separation. It is probably due to a combination of all these causes that separation does not occur.

In conclusion, I should like to express my thanks to Prof. Lindemann, to Mr. A. C. Egerton, and to Mr. I. O. Griffith for constant help and advice during this work, and to the Scientific and Industrial Research Board for a grant whereby it has been possible to carry it out.

Summary.

(1) Formulæ are derived for the migration velocities of ions which differ in mass but which are otherwise identical.

(2) As a result of these formulæ, the possibility of separating isotopes by differences of migration velocities is discussed.

(3) Two series of experiments are described in which chlorine ions in the one case and magnesium ions in the other are made to migrate in a jelly of agar-agar under conditions judged to be suitable for separation.

(4) Atomic weight determinations, carried out by methods devised for the comparison of the products so obtained, indicate that no appreciable separation has been effected.

(5) The failure of the method to yield separation is discussed.

Clarendon Laboratory,
Oxford.
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XC. *Chemical Affinity and Electronic Structure.*—Part II. *The Polar Link.* *By* BERNARD HOWELL WILSDON *.

IN a recent paper (Phil. Mag. Feb. 1925, p. 354) the author has developed a tentative theory of the energetics of the non-polar link on the basis of a quantum mechanism similar to that which has successfully explained the anomalous magnetic resolution of doublet and triplet spectral lines. It was there stated that an explanation of the polar type of combination followed in an analogous manner by the substitution of the Stark effect due to an electrostatic field for the magnetic field of the non-polar molecule. The fundamental argument is essentially the same in the two cases. It is assumed that a necessary condition for a stable molecular combination is that the frequencies of the valency orbits concerned shall be synchronized. If ν_1 and ν_2 represent the frequencies of the valency electrons of the combining atoms in their ground orbits, $h(\nu_1-\nu_2)$ represents a quantum of energy which is termed the available energy of accommodation, E_a. This energy is supposed to be responsible for the changes involved in the transfer of a valency electron or electrons from the positive to the negative atom, and for the potential energy of valency electrons and "trunk" in the field of the stripped positive ion. The change in frequency of the valency orbits produced under these conditions, multiplied by the unit of action, h, must then represent the change in kinetic energy. If we know the ratio of the kinetic to total energy in the field of the molecule, we can then calculate the total energy change which must be equal to the heat of formation. This ratio is known as a result of a theorem of Bohr (Phil. Mag. xxvi. p. 24, 1913). In a Coulomb field

$$E_{kin} = -\tfrac{1}{2}E_{pot},$$

so that

$$Q = \Delta W = \Delta E_{kin} + \Delta E_{pot} = -\Delta E_{kin}.$$

In order to determine the distribution of the available energy of accommodation in the molecule, it is necessary to make assumptions as to the changes in quantum numbers which will define the electrostatic moment of the charged elements of structure. Just as the magnetic moment of an electronic orbit is quantized in terms of the Bohr, the electrostatic moment must be a multiple or sub-multiple of the quantity $\frac{3h^2}{8\pi^2 meZ_e}$. Here Z_e is the effective atomic number, and the other symbols have their usual significance. If x represents the time mean displacement of an electron in the direction of a field F, its moment will be xe, and its potential energy xeF. As shown by Sommerfeld ('Atomic Structure,' Engl. trans. p. 311), if this is equated to the change in energy produced by the imposition of a field F as calculated by Schwarzschild and Epstein in explaining quantitatively the Stark effect, we have

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* Communicated by Dr. J. W. Nicholson, F.R.S.

$$\frac{3h^2}{8\pi^2 me}\cdot\frac{F}{Z_0}(n_1+n_2+n_3)(n_2-n_1)=ex=\frac{CF}{Z_0}(n_1+n_2+n_3)(n_2-n_1), \quad \ldots\ldots \quad (1)$$

where C is constant.

The quantum numbers here employed are the parabolic; $(n_1+n_2+n_3)$ is equal to the principal quantum number, and n_3 is the equatorial which defines the moment of momentum of the electron in the meridian plane of the molecule or atom. If $n_1=n_2$, the orbit is circular and the electron does not react to the imposed field. In the isolated atom the quantum numbers change only by whole numbers; in the molecule it appears necessary to admit of changes involving half numbers, as in the magnetic field. Arguments have been advanced by Mosharrafa (Proc. Roy. Soc. A, cv. p. 641, 1924) which indicate that such changes are also possible in the atom.

The change in potential energy resulting from the molecular combination of two atoms will be made up of three parts:—

(*a*) The work resulting from bringing the valency electron of the negative atom into the field of the positive. If q' represents the quantum factor assumed by this electron after adjustment, and F′ the field of the positive ion, the work will be

$$Cq'F'/Z', \quad \ldots\ldots\ldots \quad (2a)$$

where Z′ represents the effective atomic number of the negative atom.

(*b*) The work of bringing the valency electron of the positive ion into the field of the negative. This will be similarly

$$Cq''F''/Z''. \quad \ldots\ldots\ldots \quad (2b)$$

(*c*) The work of approximating the two atomic trunks. We assume that by quantum changes in the moments of the two valency electrons a moment is conferred on the trunk of the negative ion such that it is equal to the sum of the decrements so caused. Thus, if the negative ion is characterized by a principal quantum index k, and each of the equatorial quantum numbers n_3' and n_3'' change by half units to k_3' and k_3'', the moment taken up by the trunk is assumed to be

$$k(n_3'-k_3'+n_3''-k_3'')\mathrm{C}=k\mathrm{C}.$$

The energy in the field F''' of the positive *ion* will thus be

$$k\mathrm{C}\mathrm{F}'''. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2\,c)$$

The sum of these energies will be equal to E_a, the available energy of accommodation.

The hypothesis we have made as to the frequency tuning of the two valency orbits of the negative ion gives a relation between the three fields appearing in the above equations. Let p, with the appropriate affix, represent a quantum factor characteristic of the uncombined atoms; then, on imposition of a field, the change in frequency of the orbit will be given by

$$\mathrm{F}_1=\frac{\Delta\nu\,.\,\mathrm{Z}_1}{\mathrm{C}p_1}; \quad \mathrm{F}_2=\frac{\Delta\nu\,.\,\mathrm{Z}_2}{\mathrm{C}p_2}; \quad \mathrm{F}_3=\frac{\Delta\nu\,.\,\mathrm{Z}_0}{\mathrm{C}p_1}. \quad . \quad (3)$$

Substituting the above values for the fields in the sum of equations (2), we have

$$\mathrm{E}_a=-h\Delta\nu\left\{\frac{q_1}{p_1}+\frac{q_2}{p_2}+\frac{k\mathrm{Z}_0}{p_1}\right\}. \quad . \quad . \quad . \quad (4)$$

Whence, since $\mathrm{Q}=-h\Delta\nu$, we have

$$\mathrm{Q}=-h\Delta\nu=\frac{\mathrm{E}_a}{\left\{\frac{q_1}{p_1}+\frac{q_2}{p_2}+\frac{k\mathrm{Z}_0}{p_1}\right\}}=\frac{\mathrm{E}_a}{\mathrm{D}}. \quad . \quad . \quad (5)$$

In this formula it will be noted that all the effective atomic numbers, except that which refers to the negative ion, have cancelled out. The value of the remaining constant is taken as 4·195; this corresponds with the effective charge of a nucleus with 7 positive charges corrected for a screen of 8 electrons. For 8 electrons the Sommerfeld screening number is equal to 2·805; the effective atomic number of a halogen ion is thus 7−2·805 or 4·195.

In order to apply the above relations to the calculation of heats of formation of polar compounds, we must first investigate the form of the quantum factors p and q. According to the theory of the Stark effect, the change in energy of an orbit under the influence of a field F is given by equation (1) above. For a change in free energy corresponding with emission or absorption of a spectral line, the change in frequency must depend upon the difference of two terms—*i.e.*, the change in kinetic energy must be given by

$$h\Delta\nu=\frac{h\text{CF}}{\text{Z}}\{(n_2-n_1)(n_1+n_2+n_3)-(k_2-k_1)(k_1+k_2+k_3)\}$$
$$=\frac{h\text{CF}}{p}, \quad . \quad . \quad . \quad (6)$$

where the n's refer to the final state and the k's to the initial.

There are two possible types of quantum jump corresponding with this emission or absorption. In the first the equatorial quantum number n_3 remains unaltered. This, according to the theory of the Stark effect, corresponds with a parallel polarized light wave; it is one of the great triumphs of the theory that this prediction is constantly verified by spectral evidence. In molecular combination it will then be justifiable to assume that a quantum change which will produce in the free atom a parallel polarized ray will result in an orientation of the orbit which is parallel with the field of the second atom.

In the second type the equatorial quantum number jumps by one unit, so that $n_3=k\pm1$. The light is then polarized in a direction perpendicular to the field, and we shall consequently assume that the orbit is arranged in a plane at right angles to the field of the second atom. If these suppositions are true, we may expect two distinct types of polar compounds. Experimental results appear to support the prediction; it will be seen that the distinction arranges elements into classes which correspond with the A and B subgroups of the periodic table.

If the quantum factor p of the valency orbit of the atom is not equal to zero, *i.e.* if $(n_2-n_1)(n_1+n_2+n_3)\neq0$, the change in frequency resulting by increasing the field from zero to F will be given by

$$\Delta\nu=\frac{\text{CF}}{\text{Z}}\cdot p-0=\frac{\text{CF}}{\text{Z}}(n_2-n_1)(n_1+n_2+n_3). \quad . \quad (7)$$

This corresponds with parallel orientation, since n_3 the equatorial quantum number has not changed. This condition appears to be characteristic of the A group of the periodic table—*i.e.*, those elements which in the ionic form are surrounded with a complete valency shell of eight electrons. If the electronic orbit has zero moment, *i.e.* if $p=0$, no change in frequency can result on application of the field. The emission must now take place in two steps: (1) activation involving increase by one unit in the quantum sum, followed by (2) resumption of an orbit characterized by the original quantum sum. The process (1) must, according to the theory of the Stark effect, involve also change in the parabolic quantum numbers, as otherwise no change in energy would result. The resulting change in frequency will correspond with the difference in the energies of these states. If the original condition is defined by the quantum factor $(n_1+n_2+n_3)(n_2-n_1)$ and $n_2=n_1$, while the second state is $(k_1+k_2+k_3)(k_2-k_1)$ where $k_1+k_2+k_3=n_1+n_2+n_3+1$, the activated atom changes to $(k_1+k_2+k_3-1)(k_2-k_1)$, whence the total change becomes (k_2-k_1). $\Delta\nu$ will then be given by

$$\Delta\nu=\frac{\mathrm{CF}}{\mathrm{Z}}(k_2-k_1).$$

Among the elements which fall into this class we must place hydrogen, since it must have the constitution 1(00), where the symbol indicates the quantum numbers $n_3(n_1n_2)$. In the halogen elements the equatorial quantum number is always 2, so the constitution of fluorine, whose quantum sum is also 2, must be 2(00). Fluorine will therefore fall into the same class. Copper, silver, gold, zinc, cadmium, and mercury are similarly assumed to have constitutions with zero moment.

The application of these relations is first made to monovalent elements of class A—viz., the alkali halides with the exception of the fluorides. In Table I. are given, in columns 2 and 4, the p constitutions assumed (the atomic quantum factors); columns 3 and 5 give the q states (the molecular quantum factors). These are obtained by change of the equatorial quantum number by $-\frac{1}{2}$ and a change in the parabolic quantum numbers compatible with the constancy of the quantum sum. D in column 6 then represents the denominator occurring in equation (5). It is to be noted that in this type of combination the principal quantum number cancels out from the denominator and numerator.

Table I.

Heats of Formation of Alkali Halides.

1.	2.	3.	4.	5.	6.	7.	8.	9.
	p.	*q*.	*p*.	*q*.	D.	E_n.	Q calc.	Q found.
LiCl	1(01)	½(0,3/2)	2(01)	3/2(0,3/2)	7·195	682·6	94·88	93·8
LiBr	,,	,,	2(02)	3/2(0,5/2)	4·348	349·9	80·48	79·96
LiI	,,	,,	2(03)	3/2(0,7/2)	3·064	196·1	64·0	61·21
NaCl	1(02)	3/2(½,2)	2(01)	3/2(0,5/2)	7·445	725·8	97·5	97·69, 97·9
,, ...	,,	3/2(0,5/2)	,,	3/2(0,3/2)	6·915	...	104·5*	...
NaBr	,,	,,	2(02)	3/2(0,5/2)	4·598	393·0	85·48	85·71, 86·1
NaI	,,	,,	2(03)	3/2(0,5/2)	3·482	239·2	68·7	69·08
KCl	1(03)	½(0,7/2)	2(01)	3/2(0,3/2)	6·861	741·4	108·0	105·61, 105·7
KBr	,,	½(0,7/2)	2(02)	3/2(0,5/2)	4·515	427·4	94·66	95·31, 95·6
KI	,,	½(½,3)	2(03)	3/2(½,3)	3·065	254·3	82·98	80·13

In column 7, E_a gives the available energy of accommodation calculated in kilogram calories per molecule according to the equation

$$E_a = A\left(\frac{Z_1^2}{n_1^2} - \frac{Z_2^2}{n_2^2}\right). \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Here $A = \frac{hR_0L}{J}$; h is the constant of action, R the Rydberg constant, L Avogadro's number, and J the mechanical equivalent of heat, whence substituting the appropriate values $A = 310{\cdot}2$ Cal. Column 9 gives the experimental values of the heats of formation; these are taken from Landolt and Börnstein's Tables (5th edition); where divergent values are recorded, both are given. Column 8 gives the calculated heats of formation—*i. e.*, the quotient of E_a by D.

An example will make the method of calculation clear. The chlorine atom, distinguished by the asterisk in the above table, has, in the p state, the constitution 2(01); $p_2 = (n_1 + n_2 + n_3)(n_2 - n_1)$ is thus equal to 3(1). By change of $\frac{1}{2}$ unit in the equatorial quantum number the molecular quantum factor q_2 becomes 3(3/2). Of the available accommodation energy, the impulse taken up by the valency electron of the chlorine atom is thus $\frac{3(3/2)}{3(1)} \cdot h\Delta\nu$. Similarly in lithium chloride, the lithium atom has for the p state the factor 2(1) and in the q state 2(3/2), so the impulse taken up by this orbit is $\frac{2(3/2)}{2(1)} \cdot h\Delta\nu$. The impulse taken up by the trunk is then $\frac{3(\frac{1}{2}+\frac{1}{2})}{3(1)} \cdot 4{\cdot}195 = \frac{kZ_0\Delta\nu}{p}$, since the field F_3 is defined by the quantum factor of the halogen ion for which $p_2 = 3(1)$. The sum of the impulses is $7{\cdot}195\, h\Delta\nu$; E_a is given according to equation (8) by

$$310{\cdot}2\left(\frac{22{\cdot}04}{9} - \frac{1}{4}\right) = 682{\cdot}6 \text{ Cal.},$$

in which 22·04 is the square of the effective atomic number of an element of the 7th column of the periodic table, 1 the effective atomic number of the alkali, and 9 and 2 the squares of the principal quantum numbers of the chlorine and lithium atoms respectively. The quotient E_a/D 94·88 gives the theoretical heat of formation; the experimental value found is 93·8 Cal.

With sodium bromide $p_1 = 3(2)$ changes to $3(5/2)$, $p_2=4(2)$ changes to $q_2=4(5/2)$, so that D becomes

$$\frac{3(5/2)}{3(2)}+\frac{4(5/2)}{4(2)}+\frac{4\,.\,4{\cdot}195}{4(2)}=4{\cdot}598,$$

whence $Q=\dfrac{393{\cdot}0}{4{\cdot}598}=85{\cdot}48$: found 85·71 and 86·1.

With lithium bromide, sodium iodide, and potassium iodide the closest agreements with experimental values are obtained by assuming that the k_1 parabolic quantum number takes up the amount of $\frac{1}{2}$, available by decrease of the equatorial quantum number. This makes the quantum factor decrease, instead of increasing as appears usual. With sodium iodide, if we assume that the k_1 quantum number remains zero, instead of the values given in the table we shall have $D=5/2\,.\,1/2+7/2\,.\,1/3+4{\cdot}195/3=3{\cdot}765$, so that Q becomes 63·52 instead of 68·7. It will be found similarly that in the other cases the theoretical value is not altered by more than about 10 per cent. by disallowing change of the k quantum number. It is to be noted that there is no apparent reason why this change should be disallowed beyond the natural tendency to require that the distribution of impulse in apparently similar molecules should be the same. In the case of sodium chloride, good agreement is obtained by supposing that the k_2 quantum number of the halogen orbit increases by 3/2, while that of the alkali decreases by $\frac{1}{2}$. The total change is thus still unity, as our hypothesis demands. The latitude which results from the selection of a quantum factor from among several permissible values is admittedly the most unsatisfactory feature of the theory, and the accuracy of the experimental data by which it is tested is at present not sufficiently great to enable reliance to be placed on agreement between theoretical and experimental values in deciding on what quantum jumps are permissible. Moreover, it must be remembered that the introduction of the effective atomic number into our calculations can give it no more than the significance of an approximation. On the other hand, the fact that the heats of formation calculated according to different permissible quantum jumps do not greatly alter in magnitude leads to greater confidence, especially if it is recognized that it is scarcely probable that the molecule when formed is characterized by an unique electronic configuration. In fact, it seems very probable that observed heats of formation will be affected by a probability factor, and represent only a statistical average of possible changes.

It may eventually be possible to estimate these probabilities in the manner which has proved so successful in determining the intensities of electrically resolved spectral lines by the Bohr principle of correspondence.

We may now consider the data for di-atomic molecules which, on account of the electronic constitution it is necessary to assume for one of the atoms in its unexcited state, we class as type B compounds. This class will include hydrogen compounds, since in the unexcited state its quantum factor cannot be other than 1(00), and fluorine which must certainly be written 2(00). For the quantum states of the elements of the B subgroups of the first and second columns of the periodic table, it is not possible to decide with certainty. There can be no doubt, however, that these elements are assigned to their right class, since the occurrence of the principal quantum number of the negative atom in the numerator only, largely diminishes the magnitude of the heat of formation calculated according to the hypotheses we have adopted. Table II. gives the p and q values which it is necessary to assume to obtain the best agreement with the experimental values. The $p \rightarrow q$ quantum jumps, in the case of the elements of higher principal quantum number, are not always simple changes by $\frac{1}{2}$ units; it appears that the equatorial numbers may change by whole numbers in addition to the $\frac{1}{2}$ unit which seems to be a constant feature of the molecular quantum number. The regularities observed in the quantum factors assumed are sufficiently striking to remove suspicions that agreement between experimental and calculated values is merely accidental.

In each series the quantum factor for a particular element is a constant term, with the exception of silver bromide, where another permissible change gives better agreement. The term contributed by the halogen element appears to be constant throughout, except in the halogen hydracids. Hydrogen fluoride and silver fluoride are decidedly abnormal, as might have been expected, since both atoms in the undisturbed state have zero moment in the field. The chemical properties of hydrogen fluoride in particular are undoubtedly against its formulation as a polar compound. If equilibrium exists between the two forms, it must be preponderatingly in favour of the non-polar constitution. It is interesting to note that in both these abnormal cases the calculated heat of formation is very approximately one-third of that observed. This factor might be justified as proposed in Part I. of this paper (*loc. cit.*), by supposing that the ratio of kinetic to

TABLE II.

Heats of Formation of Type B Compounds.

	p_{10}.	p_1.	q_1.	p_{20}.	p_2.	q_2.	D.	E_a.	$E_a/D=Q$.	Q found.
HCl	1(00)	1(01)	1/2(1/2,1)	2(01)	...	1/2(0,5/2)	20·59	449·7	21·85	22·0 (26·0 at 2000°
HBr	"	"	"	2(02)	...	3/2(0,5/2)	13·89	114·12	8·22	8·44, 8·6
HI	"	"	"	2(03)	...	5/2(0,5/2)	11·66	−73·2	−6·28	−6·44, −6·4
HF	"	"	"	2(00)	2(01)	1/2(0,3/2)	11·89	1399·2	117·7	38·5
LiF	...	1(01)	1/2(0,3/2)	"	"	"	14·39	1632·0	113·4	114·3, 115·8
NaF	...	2(01)	3/2(0,3/2)	"	"	"	15·89	1674·8	105·4	102·6, 109·2
KF	...	2(02)	5/2(0,3/2)	"	"	"	14·39	1691·8	117·6	118·1
CuCl	2(11)	1(12)	1/2(1,5/2)	2(01)	...	3/2(0,3/2)	22·09	740·6	33·53	32·87, 35·4
CuBr	"	"	"	2(02)	...	5/2(0,3/2)	17·39	408·2	23·47	24·98
CuI	"	"	"	2(03)	...	7/2(0,3/2)	15·49	254·3	16·42	16·26, 16·9
AgF	1(22)	1(13)	3/2(0,7/2)	2(00)	2(01)	1/2(0,3/2)	17·64	1698·0	84·30	23·2
AgCl	"	"	"	2(01)	...	3/2(0,3/2)	25·84	747·6	28·94	29·38, 29·0, 29·94
AgBr	"	"	5/2(0,5/2)	2(02)	...	5/2(0,3/2)	17·64	415·0	23·52	22·7, 23·4
AgI	"	"	3/2(0,7/2)	2(03)	...	7/2(0,3/2)	18·24	261·3	14·32	13·80, 14·2, 14·99
HgCl	1(33)	2(14)	3/2(3/2,4)	2(01)	...	3/2(0,3/2)	22·92	741·4	32·35	31·3, 31·32, 32·605
HgBr	"	"	"	2(02)	...	5/2(0,3/2)	17·22	407·9	23·69	24·5, 25·475
HgI	"	"	"	2(03)	...	7/2(0,3/2)	15·33	254·3	16·59	14·2, 15·55

total energy change is characteristic of a magnetic field in which $Q=1/3\ E_{kin}$.

As an example of the calculation, we may take the case of silver bromide; the silver atom by excitation is supposed to undergo the jumps $1(22)\rightarrow 2(13)\rightarrow 1(13)$, so that F_1 is given by $\Delta\nu=\frac{CF_1}{Z_1}.(3-1)$. The molecular quantum factor, by the $\frac{1}{2}$ unit change, then becomes $5(7/2-1)$ or, what amounts to the same thing, $5(5/2-0)$, so that q_1/p_1 becomes $\frac{5(5/2)}{2}$.

The bromine atom on combination is assumed to undergo the jump $2(02)\rightarrow 3/2(\frac{1}{2},2)$ or $5/2(0,3/2)$, so that $q_2/p_2=\frac{3(3/2)}{2}$. The trunk takes up the impulse $4/2\ .\ Z_0 h\Delta\nu$, so that the total energy change becomes

$$E_a=415\cdot 0=\left\{\frac{5(5/2)}{2}+\frac{4(3/2)}{2}+4/2\ .\ 4\cdot 195\right\}.\ h\Delta\nu$$
$$=17\cdot 64\ h\Delta\nu,$$

whence $Q=23\cdot 52$: found 22·7 and 23·4 Cal., between which the theoretical value falls.

In polyatomic molecules, negative terms must enter into the denominator D on account of the energy of strain between similarly charged ions Thus, for instance, in the case of calcium chloride the available energy of accommodation must also comprise the negative work necessary for bringing the two chlorine ions into proximity. It is not at present advisable to attempt to calculate these heats until more experience has been gained of the simple diatomic compounds. It is interesting to note, however, that the same general relations between elements of the A and B subgroups are evident as were observed before. The denominator D for the B subgroup is always much greater than that of the A subgroup. With increasing values of the principal quantum number the denominator for the halides of group B elements decreases much less with increase in atomic weight of the halide than in the A group, where the ratios are approximately of the same order. This must undoubtedly be due to the constant term contributed by the positive ion which is proportional to its principal quantum number; the denominator as a whole

TABLE III.

Heats of Formation of the Halides of Divalent Elements.

Principal quantum no.	E_a.	GROUP A.			GROUP B.		
			Q found.	D.		Q found.	D.
2	522·5	$BeCl_2$	155·0	3·37	...	...	...
3	654·4	$MgCl_2$	151·01	4·33	...	...	...
	322·0	$MgBr_2$	121·7	2·65	...	...	...
	168·2	MgI_2	84·8	1·98	...	...	...
4	700·8	$CaCl_2$	183·89 190·3	3·75	$ZnCl_2$	97·21 97·4	7·20
	368·2	$CaBr_2$	154·92	2·38	$ZnBr_2$	75·93 76·0	4·85
	214·5	CaI_2	149·01	1·44	ZnI_2	49·231	4·36
5	721·8	$SrCl_2$	184·56 184·7	3·91	$CdCl_2$	93·24	7·74
	389·3	$SrBr_2$	157·70 158·1	2·47	$CdBr_2$	75·20 76·3	5·14
	235·5	SrI_2	122·9	1·92	CdI_2	48·82	4·82
6	733·6	$BaCl_2$	196·88 197·1	3·72	...	...	...
	401·0	$BaBr_2$	172·1 172·4	2·33	...	...	...
	247·3	BaI_2	136·1	1·82	...	...	...
7	741·4	...	...	...	$HgCl_2$	53·3 54·49	13·60
	407·9	...	...	...	$HgBr_2$	40·5 40·6 41·88	9·73
	254·3	...	...	...	HgI_2	25·2	9·81

thus becomes more nearly constant. This can be seen from an inspection of Table III., where the quotients of E by the mean value of the experimental heats of formation are compared.

Simla,
October 1924.

XCI. *The Motion of an Electric Charge.* *By* ARTHUR BRAMLEY, *Ph.D., Fellow in Physics, Princeton University* *.

ANY discussion of the motion of electric charges must be based on the fundamental laws of electrodynamics as developed into their final state by Maxwell. The consideration of the relation of the charge to the electric and magnetic field is based on experimental laws:

$$\int \mathrm{H}x\,dx+\mathrm{H}y\,dy+\mathrm{H}z\,dz=\iint\left(\rho v+\frac{d\mathrm{E}}{dt}\right)_n d\mathrm{S}, \quad . \quad \text{(i.)}$$

where the line integral is taken over any particular closed curve, and the surface integral over any surface bounded by this curve, where H = magnetic field, E = electric field, ρv = electric flux through the surface at any point, and n denotes the normal component

$$\int \mathrm{E}x\,dx+\mathrm{E}y\,dy+\mathrm{E}z\,dz=-\iint\left(\frac{d\mathrm{H}}{dt}\right)_n d\mathrm{S}. \quad . \quad . \quad \text{(ii.)}$$

If we know ρv as a continuous function of position at any particular instant t, we can write the above equations in the well-known form

$$\left.\begin{aligned}\rho u+\frac{\partial \mathrm{E}_x}{\partial t}&=\mathrm{curl}_x\mathrm{H},\\ -\frac{\partial \mathrm{H}_x}{\partial t}&=\mathrm{curl}_x\mathrm{E},\end{aligned}\right\}\text{etc.}, \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

where u = the component along the x-axis.

Now, as Einstein has pointed out (Berlin Academy, January 1924), these equations define a relation between the field and the charge at any given instant, but do not correlate the different images of the electromagnetic phenomena at any instant t with that at any other instant t'.

Let us consider a four-dimensional manifold (x, y, z, t) where x, y, z are the space coordinates and t the time coordinate, and where

$$ds^2=dx^2+dy^2+dz^2-dt^2,$$
$$c^2=1,$$

as in special relativity.

Then the fundamental integrals and hence Maxwell's equation refer to any space-like variety

$$d\bar{s}^2=dx^2+dy^2+dz^2,$$

obtained by taking a section perpendicular to the time-axis.

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* Communicated by the Author.

The electric flux ρv will be a function of position in any one variety

$$t=t_0,$$

$$(\rho v)=f(x, y, z),$$

and hence can be expressed as a function of position in the four-dimensional space

$$(\rho v)=f(x, y, z, t).$$

Now, if there are no point charges in the field, *i. e.* singularities, we can expand the flux as a function of the time, *e. g.*,

$$(\rho u)=(\rho u)_0+(\rho u)_1 t+(\rho u)_2 t^2+\ldots\ldots,$$

where $(\rho u)_0$, $(\rho u)_1$, and $(\rho u)_2$, etc.,

are functions of (x, y, z).

Further, we can expand E and H as a power series in t,

$$E=E_0+E_1 t+E_2 t^2+E_3 t^3+\ldots.,$$

$$H=H_0+H_1 t+H_2 t^2+H_3 t^3+\ldots.,$$

where E_0, H_0, E_1, H_1, etc., are functions of x, y, and z only, and where E and H represent any one of the three components E_x, H_x, etc., the distribution of charge and velocity being of such a nature that the series are convergent.

Taking the case of motion along the x-axis, we get, by substituting in Maxwell's equation,

$$\begin{aligned}&(\rho u)_0+(\rho u)_1 t+(\rho u)_2 t^2+\ldots.\\&+E_1+2E_2 t+3E_3 t^2+\ldots.\\&=\text{curl}\,H_0+\text{curl}\,H_1\,.\,t+\text{curl}\,H_2\,.\,t^2+\ldots.\end{aligned}$$

Since these equations must be valid for all values of t, we have

$$\begin{aligned}&(\rho u)_0+E_1=\text{curl}\,H_0,\\&(\rho u)_1+2E_2=\text{curl}\,H_1,\\&(\rho u)_n+(n+1)E_{n+1}=\text{curl}\,H_n,\end{aligned}$$

where

$$(\rho u)=(\rho u)_0+(\rho u)_1 t+\ldots.$$

Similarly, for the second set of Maxwell's equations,

$$\begin{aligned}H_1&=\text{curl}\,E_0,\\2H_2&=\text{curl}\,E_1,\\(n+1)H_{n+1}&=\text{curl}\,E_n.\end{aligned}$$

For points where $\rho=0$ for all values of t,

$$E_1=\operatorname{curl} H_0,$$

$$E_{2n}=\frac{\pm}{\underline{|2n}}\nabla_1^2 \ldots \nabla_n^2 E_0,$$

$$E_{2n-1}=\frac{\mp}{\underline{|2n-1}}\nabla_1^2 \ldots \nabla_{n-1}^2 E_1,$$

and a similar set of equations for H. These equations allow us to determine all the subsequent coefficients from the knowledge of E_0 and H_0, E_0 and H_0 being the values of the two field intensities at a particular instant when

$$t=0.$$

These equations (iii.) are subject, however, to certain kinematic conditions determined by the nature and motion of the electric charges. In the classical method of solution of Maxwell's equations developed by Kirchhoff, the magnetic and electric forces are given by the equations

$$H=\operatorname{rot}\psi,$$

$$E=-\frac{\partial\psi}{\partial t}-\operatorname{grad}\phi,$$

where

$$\phi=\frac{1}{4\pi}\iiint\frac{\rho'}{r}\,dx\,dy\,dz,$$

$$\psi=\frac{1}{4\pi}\iiint\frac{(\rho v)'}{r}\,dx\,dy\,dz,$$

where the dash denotes that in carrying out the integrations the values of ρ and ρv, respectively, at the time $t=-r$ previous to that for which the integrals are being evaluated, have to be substituted.

Suppose that the electric flux (ρv) is moving along the x-axis, being defined by the equation of propagation

$$\rho u=f\{x-at^n\},$$

then

$$(\rho u)'=f\{x-a(t-r)^n\};$$

whence

$$\left[\frac{\partial^m(\rho u')}{\partial t^m}\right]_{t-r=0}=0, \qquad m<n,$$

where

$$\left[\frac{\partial^n(\rho u)'}{\partial t^n}\right]_{t-r=0}=f'(x)=\frac{\partial f}{\partial\{x-a(t-r)^n\}}.$$

In the case where the density ρ is different from zero only at and in the neighbourhood of a point, the equation

$$(\rho u)=f\{x-at^n\}$$

defines the motion of the point charge according to the equation

$$x-at^n=\text{const.}=A;$$

for if we consider the motion of the maximum value of the flux, *i. e.* the flux at the position of the charge, we see that it is defined by

$$(\rho u)_{\text{max.}}=f(A),$$

where

$$A=x-at^n,$$

being the value for which $f(y)$ is a maximum.

If $n=2$, the motion of the charge is uniformly accelerated.

If we consider the motion of a charge whose density is different from zero only at and in the neighbourhood of a certain point, fixed or moving, then from the definition of H we see that since in this case we can regard (ρu) as a function of the form,

i. e.,

$$\rho u=(\rho u)_0+(\rho u)_n t^n+\ldots$$

$$(\rho u)_i=0, \quad i=1\ldots . x-1,$$

so that the first $n-1$ time-derivatives of the magnetic intensity are zero along the light-cone

$$(x-x')^2+(y-y')^2+(z-z')^2=t^2$$

for any position (x', y', z', t') of the electric charge. As the charge moves along, the conic surface will describe a continuous parametric family of surfaces over which the above derivatives are zero. Since the derivatives which are continuous functions of position are zero throughout the column generated by the cone, they must be zero for all points in space. Hence

$$\frac{\partial^m H}{\partial t^m}=0, \quad m<n,$$

or

$$H_i=0, \quad i=1\ldots . n-1.$$

(See note p. 922.)

For the case where the charge is stationary or moving with uniform rectilinear motion, the expansions are not subject to any kinematic conditions. Let us therefore consider the case of uniform accelerated motion,

then
$$\rho u = f(x - at^2)\,;$$
$$H_1 = 0\,;$$
i. e.,
$$\operatorname{curl} E_0 = 0.$$

Let us assume that initially the solution has the form

$$E_{0x} = \frac{ex}{r^3} + \chi_x, \quad E_{0y} = \frac{ey}{r^3} + \chi_y, \quad E_{0z} = \frac{ez}{r^3} + \chi_z,$$

where χ is an arbitrary function which has to be determined.

Since
$$\operatorname{curl} E_0 = 0$$
and
$$\operatorname{div.} E_0 = 0 \quad \text{where} \quad \rho = 0,$$
we have that
$$\chi_x = \frac{\partial \chi'}{\partial x}, \quad \chi_y = \frac{\partial \chi'}{\partial y}, \quad \chi_z = \frac{\partial \chi'}{\partial z},$$
where
$$\Delta^2 \chi' = 0.$$

If we consider the radiation from this system defined by Poynting's vector,

$$\Pi_x = E_{0y} H_{0z} - E_{0z} H_{0y},$$
$$\Pi_y = E_{0z} H_{0x} - E_{0x} H_{0z},$$
$$\Pi_z = E_{0x} H_{0y} - E_{0y} H_{0x},$$

since the terms in higher powers of t contain higher powers of $\frac{1}{r}$, being derivatives of H_0 and E_0 respectively, we see that the radiation must be zero, since E_0 is derived from a potential function, *i. e.*,

$$E_{0x} = \frac{\partial V}{\partial x}, \quad E_{0y} = \frac{\partial V}{\partial y}, \quad E_{0z} = \frac{\partial V}{\partial z};$$

so that the system in uniform accelerating motion can never radiate energy when obeying the classical electrodynamical laws.

From the above discussion we see that the classical radiation field developed from Kirchhoff's solution of Maxwell's equations can only be regarded as a fictitious solution which contains no energy; in the gravitational field several examples of fictitious fields have been pointed out by

Eddington, while Bohr has developed the consequences of the idea applied to electromagnetic theory *.

Let us next consider the motion of an electric charge obeying the familiar laws of electrodynamics, and hence radiating no energy.

The equation of motion of the charge *e* in the Riemannian space

$$ds^2 = g_{ij}\, dx^i\, dx^j$$

is

$$\frac{ds}{dt}\left(m \cdot \frac{dt}{ds}\right)\left[\frac{d^2x^2}{ds^2} + \Gamma^2_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}\right] = F'^2_\alpha \frac{dx^\alpha}{dt}, \quad . \quad \text{(A)}$$

where $\Gamma^2_{\alpha\beta}$ is the Christoffel symbol and F'^2_α the component of force acting on the charge.

Since

$$\frac{ds}{dt} = \frac{ds}{dx^4},$$

we have

$$\frac{d^2x^2}{ds^2} + \Gamma^2_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds} = \frac{F'^2_\alpha}{m}\frac{dx^\alpha}{ds}\cdot\frac{ds}{dx^4}.$$

Let

$$\frac{dx^i}{ds} = \phi^i \cdot \dot{x}^4, \quad \dot{x}^i = \frac{dx^2}{ds}, \quad i = 1 \ldots . 4,$$

$$\phi^4 \equiv 1\,;$$

then we get

$$\phi^i \cdot \ddot{x}^4 + \frac{\partial \phi^i}{\partial x^\alpha}\,\phi^\alpha(\dot{x}^4)^2 + \Gamma^i_{\alpha\beta}\phi^\alpha\phi^\beta(\dot{x}^4)^2 = \frac{F'^i_\alpha}{m}\phi^\alpha,$$

or

$$\ddot{x}^4\phi^i + (\dot{x}^4)^2\left\{\frac{\partial\phi^i}{\partial x^\alpha}\phi^\alpha + \Gamma^i_{\alpha\beta}\phi^\alpha\phi^\beta\right\} - \frac{F'^i_\alpha}{m}\phi^\alpha = 0,$$

$$i = 1 \ldots . 4.$$

These four equations allow us to solve for the four unknowns

$$\dot{x}^4, \quad \phi', \quad \phi^2, \quad \text{and} \quad \phi^3.$$

Knowing this solution, we can write our equation in the form

$$\frac{d^2x^i}{ds^2} + \left\{\Gamma^i_{\alpha\beta} - \frac{F'^i_\mu \phi^\mu}{m} g_{\alpha\beta}\right\}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds} = 0,$$

or

$$\frac{d^2x^i}{ds^2} + G^i_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds} = 0, \quad . \quad . \quad . \quad . \quad . \quad \text{(B)}$$

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* Bohr, Kramer, and Slater, Phil. Mag. xlvii. p. 785 (1924).

where

$$G^i_{\alpha\beta} = \Gamma^i_{\alpha\beta} - \frac{F'^i_\mu \phi^\mu}{m} g_{\alpha\beta}$$

for

$$1 = g_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}.$$

The equation (A) gives

$$\frac{dx^i}{ds} = \psi^i(s),$$

where s is the parameter along the path.

But $s=\chi(x)$, a function of position on the curve, allows us to write

$$\frac{dx^i}{ds} = f'(x);$$

so that ϕ^i is a function of $(x^1 \ldots . x^4)$ only.

Thus, in equation (B) the $G^i_{\alpha\beta}$ is a function, not only of position but also of the particular path. This leads to a more generalized geometry than the geometry of paths, considered by Eisenhart and Veblen, in which $\Gamma^2_{\alpha\beta}$ is a function of position only. Whence we are led to a result analogous to the fundamental assumption (L. P. Eisenhart, Nat. Academy, June 1923) that the motion of electrons manifests itself in paths in a space-time continuum of four dimensions.

We shall not consider an application of the ideas involved above to the case of a charge moving geodesically (in a particular path) in the space with linear element

$$-ds^2 = \left(1-\frac{2e}{r}\right)^{-1} dr^2 + r^2\, d\theta^2 + r^2 \sin^2\theta\, d\phi^2 - \left(1-\frac{2e}{r}\right) dt^2,$$

where e = a constant depending on the charge at the origin of coordinates which produces the field.

If we wish to make the electron stationary in the field at any point, we must apply an external force to it which will become equal and opposite to the fictitious field due to the metric when the electron becomes at rest.

The equation representing the stationary electron at any point in space is therefore

$$g_{ij}\left(\frac{d^2x^j}{ds^2} + G^j_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}\right) = \psi_i,$$

where

$$\psi_i = -F_{ik}J^k/_\beta,$$

$$\beta = \frac{dt}{ds},$$

where F_{ik} represents the forces due to the field of the metric.

Since

$$\frac{dx'}{ds} = \frac{dx^2}{ds} = \frac{dx^3}{ds} = 0 \quad \text{and} \quad \frac{dx^4}{ds} = 1$$

when the electron is stationary, we get

$$g_{ij}G^j_{44} = \psi_i = F_{ik}J^k/_\beta.$$

The only equation not zero is

$$g_{11}G'_{44} = \psi_1 = -F_{14}(-\epsilon)$$

or

$$G'_{44} = \left(\frac{2e}{\epsilon}\right)\frac{-\epsilon}{r} = \epsilon F_{14}.$$

Thus

$$2e = \epsilon^2,$$

where

$$\epsilon = \text{charge on nucleus} = \text{charge on electron.}$$

Thus the law of force is the well-known inverse square law; *i.e.*, the fictitious forces due to the metric make the path of the charge (electron here considered) equivalent to that of a charge in flat space under the influence of Coulomb's law.

The same problem has been considered by the author (Proc. Nat. Acad., Aug. 1923, "Motion of an Electric Particle in a Riemann Space") for an infinitesimal particle where the same conclusions were reached regarding the motion.

In this section we have considered the motion of any electric charge without radiation of energy, and find that we can express the equations of motion in the form

$$\frac{d^2x^2}{ds^2} + G^2_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds} = 0,$$

where $G^2_{\alpha\beta}$ depends not only on a point function, but also *on the character of the path of the charge.* If we can write the energy tensor in the form of squares, then

$$ds^2 = g_{11}dx_1{}^2 + g_{22}dx_2{}^2 + g_{33}dx_3{}^2 + g_{44}dx_4{}^2,$$

where

$$g_{ii} = g_{ii}(x^1, x^2, x^3, x^4, \alpha_{ii}),$$

where α_{ii} depends on the trajectory, the α's being different for different paths. These parameters, the α's, are closely connected with the quantum numbers which serve to define the equations of motion when written in integral form.

Lastly, the above analysis is applied to the simple linear element

$$-ds^2 = \left(1-\frac{2e}{r}\right)^{-1} dr^2 + r^2 d\theta^2 + r^2 \sin^2\theta\, d\phi^2 - \left(1-\frac{2e}{r}\right) dt^2,$$

where the α's have been left arbitrary, since they can only modify the form of the function representing the force by a constant multiplier.

We are next going to consider the most general motion of a charge radiating no energy but under the influence of Maxwellian forces, and also a resisting force proportional to the velocity [*].

The equation of motion is, therefore,

$$\ddot{x}^2 + \Gamma^2_{\alpha\beta}\dot{x}^\alpha \dot{x}^\beta - G\dot{x}^2 = 0,$$

where G is a scalar proportionality factor.

The scalar G can, however, be written in the form

$$G = G_{\alpha\beta}\dot{x}^\alpha \dot{x}^\beta,$$

where $G_{\alpha\beta}$ is a function of position only.

Let us then consider a set of paths defined by the n equations

$$\ddot{x}^i + \Gamma^i_{\alpha\beta}\dot{x}^\alpha \dot{x}^\beta - \dot{x}^i G_{\alpha\beta}\dot{x}^\alpha \dot{x}^\beta = 0, \quad . \quad . \quad . \quad \text{(I.)}$$

where $\Gamma^2_{\alpha\beta}$ and $G_{\alpha\beta}$ are tensor functions of position only.

The condition that the equation (I.) has a solution of the form

$$e^{\int \phi_\alpha dx_\alpha} g_{\alpha\beta}\dot{x}^\alpha \dot{x}^\beta = \text{const.} \quad . \quad . \quad . \quad . \quad \text{(II.)}$$

is that

$$[grs/t + 2g\alpha r\, Gst\, \dot{x}^\alpha + \phi r gst]\, \dot{x}\, \dot{x}^s \dot{x}^t \equiv 0.$$

A particular solution of this is

$$\begin{aligned} Grs/t\, \dot{x}^r \dot{x}^s \dot{x}^t &\equiv 0, \\ Gst &= gst, \\ \phi_r &= -2g_{\alpha\beta}\dot{x}^\alpha. \end{aligned}$$

Thus a particular solution of equation (I.) is

$$e^{\int G_{\alpha\beta}\dot{x}^\alpha d\dot{x}^\beta} G_{\alpha\beta}\dot{x}^\alpha \dot{x}^\beta = \text{const.} = A, \quad . \quad . \quad . \quad \text{(II'.)}$$

the integral being taken along a path.

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[*] Richardson, 'Electron Theory,' p. 266.

(I.) may also be written in the form

$$\ddot{x}^i+\Gamma^i_{\alpha\beta}\dot{x}^\alpha\dot{x}^\beta = A\,e^{-\int G_{\alpha\beta}\dot{x}^\alpha dx^\beta}\,.\,\dot{x}^i.$$

Let us next consider a change from the parameter s to t; our equation (I.) becomes

$$\left(\frac{dt}{ds}\right)^2\left[\frac{d^2x^i}{ds^2}+\Gamma^i_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}\right]$$
$$=\left(\frac{dt}{ds}\right)^3 G_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}\frac{dx^i}{ds}-\frac{d^2t}{ds^2}\frac{dx^i}{ds}.$$

If

$$\frac{d^2t}{ds^2}\Big/\left(\frac{dt}{ds}\right)^3 = G_{\alpha\beta}\frac{dx^\alpha}{dt}\frac{dx^\beta}{dt}$$

or

$$\frac{dt}{ds} = e^{3\int G_{\alpha\beta}\frac{dx^\alpha}{ds}dx^\beta},$$

then our equation can be written in the geodesic form,

$$\frac{d^2x^i}{ds^2}+\Gamma^i_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds}=0. \quad . \quad . \quad . \quad . \quad (\text{III.})$$

Equation (II′.) can then be written in the form

$$\frac{dt}{ds}G_{\alpha\beta}\dot{x}^\alpha\dot{x}^\beta = A,$$

or the solution of (III.) is

$$\left(\frac{dt}{ds}\right)^3 G_{\alpha\beta}\frac{dx^\alpha}{dt}\frac{dx^\beta}{dt} = A.$$

Now

$$e^{3\int G_{\alpha\beta}\frac{dx^\alpha}{dt}\left(\frac{dt}{ds}\right)dx^\beta} = e^{3\int G_{\alpha\beta}\frac{dx^\alpha}{dt}\frac{dx^\beta}{dt}\left(\frac{dt}{ds}\right)dt};$$

$$\therefore \quad e^{3\int G_{\alpha\beta}\frac{dx^\alpha}{dt}\frac{dx^\beta}{dt}\left(\frac{dt}{ds}\right)dt}\,.\,G_{\alpha\beta}\frac{dx^\alpha}{dt}\frac{dx^\beta}{dt} = A$$

is the form of the solution of (III.).

If $G_{\alpha\beta} = m\,\bar{g}_{\alpha\beta}$,

m = invariant mass,

then

$$M = m\frac{dt}{ds} = \text{relative mass}.$$

Thus we can write our solution in the form

$$e^{3\int M\bar{g}_{\alpha\beta}\frac{dx^\alpha}{dt}dx^\beta} \cdot \bar{g}_{\alpha\beta}\frac{dx^\alpha}{dt}\frac{dx^\beta}{dt} = \frac{A}{m}.$$

But since

$$e^{\int M\bar{g}_{\alpha\beta}\frac{dx^\alpha}{dt}dx^\beta} = e^{\Sigma \text{ Action}},$$

we see that for any periodic path the Σ Action must be periodic ; *i. e.*,

$$\int M g_{\alpha\beta}\frac{dx^\alpha}{dt}dx^\beta = 2\pi n i, \qquad i = \sqrt{-1}, \quad n = \text{integer}.$$

Thus if we consider the most general motion of an electric charge without radiation of energy, we find that the motion is periodic only in case the following condition is satisfied :

$$\Sigma \text{ Action} = nh,$$

where $n = \text{integer}$,

$h = \text{constant}$,

the action integrals being taken over a complete cycle.

The Quantum Conditions for periodic orbits are a particular case of this more general condition.

In conclusion, the writer wishes to express his gratitude to Professors E. P. Adams and L. Eisenhart for their interest and assistance during the writing of this paper.

Note (see page 915).—If we expand the potential ψ in Kirchhoff's solution in powers of $(t-r)$, we find that ψ is of the form,

$$\psi = \frac{1}{4\pi}\iiint\Big[f_1(x, y, z) + f_2(x, y, z)'(t-r)^n$$

$$+ \text{terms in higher powers of } (t-r) \qquad \Big] dx, dy, dz,$$

where x, y, and z are independent of t,

for $(\rho u)' = (\rho u)_0 + (\rho u)_n (t-r)^n + \ldots\ldots$

$(\rho u)_i = \text{function of } x, y, z \text{ only},$

and $r' = \sqrt{(\xi-\alpha)^2 + \beta^2 + \gamma^2},$

where $\xi = A - a(t-r)^n$ from the equation of motion of the charge, and α, β, γ are the coordinates of the point where ψ is evaluated, where r=distance between position of electron at time t and point (α, β, γ).

Since $\mathrm{H}=\mathrm{rot}\,\psi$,

we find
$$\frac{\partial^m \mathrm{H}}{\partial t^m}=\mathrm{rot}\frac{\partial^m \psi}{\partial t^m}=0, \quad m<n,$$
for
$$r-t=0.$$

XCII. *A Possible Reconciliation of Bohr's Interpenetration Ideas with Sommerfeld's Relativistic Treatment of Electron Orbits.* By R. A. Millikan *and* I. S. Bowen[*].

I. *Introduction.*

IN a preceding article[†] we have presented a dilemma, each horn of which involves an inadmissible conclusion, and we have thus far suggested no way out of the difficulty.

The first purpose of this paper is to indicate the nature of the new assumption which it seems to us necessary to make in order to obtain some sort of a consistent scheme of interpretation, and the second purpose is to discuss the experimental data which lend some support to this assumption.

II. *Statement of the Dilemma.*

Our former work has shown that both the regular and the irregular doublet laws which had their origins in the study of X-rays are also valid throughout the whole field of optics. This fact leaves no alternative save to consider the s terms in optics as corresponding completely with the $\mathrm{L_I}$ $\mathrm{M_I}$ etc. terms in X-rays, the p_2 terms in optics with the $\mathrm{L_{II}}$ $\mathrm{M_{II}}$ terms in X-rays, and the p_1 terms in optics with the $\mathrm{L_{III}}$ $\mathrm{M_{III}}$ terms in X-rays. No escape from this conclusion, drawn in our former paper, seems to us to be possible.

In order to bring out sharply the nature of the difficulty which this last conclusion involves, we shall at first confine attention to orbits of total quantum number 2. The foregoing identification of optical and X-ray levels means definitely, as applied to these orbits, either (1) that we must adopt the choice made in optics and regard the L_{II} L_{III} orbits as both circles (2_2 orbits), such as the p_1 p_2 orbits are usually supposed to be in optics, or else (2) that we must adopt the choice heretofore made in X-rays and regard p_1 p_2 as two orbits of the shape 2_2 and 2_1, respectively, thus making the s and the p_2 orbits of the same shape, *i. e.* of shape 2_1.

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[*] Communicated by the Authors.

[†] Phys. Rev. xxiv. p. 223 (1924).

The objection to the first choice is that it makes L_I an ellipse of shape (2_1), and L_{II} a circle of shape 2_2, and then, in the case of the higher atomic numbers, the separation of these two energy-levels which is required by the application of the relativity principle (change of mass with speed) is about four times as great as the observed separation. Further, the screening constant of the circle should be greater than that of the ellipse, because of the greater penetration of the latter inside the screening electrons, so that the actual separation between the L_I and L_{II} levels should be larger than the relativity difference by the difference in the screening constants of the differently shaped orbits.

These considerations seemed so compelling that we said in the preceding article that there seemed to be no escape except to deny the applicability of the relativity principle *in toto* to electronic orbits. In view, however, of the complete quantitative success of this principle, especially in the interpretation of the behaviour of the spectra of atomic hydrogen and ionized helium, this denial seems well-nigh impossible.

The second choice, on the other hand, appears altogether impossible for a number of reasons, the most cogent among which is the fact, reported in our preceding paper, that we find that *the separation of the triplets as well as doublets for a series of atoms of like electronic structure but varying nuclear charge follows the relativity law.* Since the writing of the preceding paper many new triplets have been studied, and they completely bear out our former assertion as to the applicability of the relativity formula.

Since now in the second quantum state there are but two possible shapes of orbits (azimuthal quantum numbers) 2_1 and 2_2 to manipulate, it is absolutely necessary to call upon some *inner* quantum number—*i. e.*, some new orientation without change in shape—to account for at least one of the three energy levels here involved. *If, then, inner quantum numbers must be invoked anyway, it is in the interest of simplicity and consistency to invoke them throughout in explaining the behaviour of both triplets and doublets.* This argument seems to us an altogether conclusive one against the adoption of the change in azimuthal quantum number to account for the difference in the p_1 p_2 energy levels.

III. *A Third Possibility.*

Since both of our suggested alternatives appear then impossible, our only escape is to find some break in the continuity of the proof of the exact applicability of the relativity formula to the atoms from uranium down to hydrogen.

To state our present conclusion in a word, we are herewith pointing out that it is just possible to make such a break between ionized helium and lithium, and thus save the relativity explanation for simple nucleus-electron systems like hydrogen and ionized helium, where, as a matter of fact, the evidence for the validity of the relativity formula is wonderfully exact.

In order to do this, however, we are forced to make a very difficult and strange assumption, viz.: that the remarkable fitting of all our data into the relativity formula for all the atoms from lithium up to chlorine, and then throughout the whole X-ray field, is accidental, and that there must be some other cause of a non-relativistic sort which is responsible for the behaviour of the spectra of all these elements, a cause which, though it has to do with changes in inner quantum numbers rather than azimuthal, yet leads not only to a fourth-power law, as does the relativity cause, but also to a formula having very closely the same numerical constants as has the relativity law.

To state the situation slightly differently, despite the fitting of the relativity law with the experimental data from lithium to uranium, we now throw overboard in all this field the relativity explanation of the observed doublet and triplet separations. We retain in both the field of optics and that of X-rays the optical selection principle, and make both p_1 p_2 and L_{II} L_{III} differ in inner quantum number, while the s and the p_2 levels, as well as the L_I L_{II} levels, differ in azimuthal quantum number. At the same time we save the relativity explanation of the separation of the doublet of hydrogen and of ionized helium.

Landé * and others have before made this same choice to the extent of insisting that the selection principle used in optics be used also in the field of X-rays, but in so doing they have not been confronted with the new evidence contained in *our* observations of the great utility of the simple Sommerfeld relativity formula in leading to correct doublet and triplet separations, so that their choice was relatively easy. Nor have they attempted to show the difficulties of the position into which we are forced by such a choice. This we endeavour to do in the present paper.

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* *Zeit. f. Phys.* xvi. p. 391 (1923); xxiv. p. 88, and xxv. p. 46 (1924).

IV. *The New Success of the Relativity Formula.*

The two striking and altogether new successes of the relativity formula as shown in our work are:—

(1) The fairly close prediction which it makes of the screening due to the two K electrons in the spectra due to stripped atoms from lithium through nitrogen. This is presented in Table I. of the article in Phys. Rev. xxiv. p. 211. Also, since this paper was read before the American Physical Society in April 1924, Landé * has made and published a similar computation, using our preliminary and much less precise data published in January 1924 †.

(2) The extraordinarily accurate prediction of the variation of doublet separation with change in *total* quantum number. This is beautifully shown in Table I., *l. c.*, where we change the numerical constant of the relativity formula from ·365 to ·108 in carrying the computation of $\Delta\nu$ from the second to the third quantum state. A somewhat less perfect example of this success is seen in Tables II., V., VII., in all of which we found the computed and observed doublet separations varying with total quantum number about as the relativity formula demands. Landé also in Table IV. (*Zeits. f. Phys.* xxiv. p. 91) displays this sort of success.

By making the choice which we have made above, and treating the $2p_1$ $2p_2$ orbits as two circles differing only in orientation (inner quantum number), we are of necessity taking the position that these two successes of the relativity formula are purely accidental; and we are tacitly assuming that there is some entirely different cause of the separation of $2p_1$, $2p_2$, etc., which leads not only to the same type of variation of $\Delta\nu$ with both atomic number and with total quantum number as does tho relativity cause, but which also leads to very nearly the same numerical constants as does the relativity cause. This is a difficult assumption to make, but there is absolutely no alternative to it if we wish to avoid both horns of the dilemma presented above. We are ourselves forced to make it, since neither of these horns appears to us admissible.

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* *Zeit. f. Phys.* xxiv. p. 32 (1924).

† Phys. Rev. xxiii. p. 33.

In making this assumption we are a little better off than we should have been in discarding the applicability of the principle of change in mass with speed altogether to electronic orbits, because we can now retain the relativity explanation of the behaviour of the hydrogen and helium spectra, where the evidence is most beautifully quantitative and where it is most difficult to conceive of any other cause.

V. *Our Assumptions and the Requirements which the New non-Relativistic Cause of Fine Structure must Meet.*

Having by this assumption separated hydrogen and helium from other atoms, it becomes our task to re-examine all of our data upon other substances in order to see how precisely our relativity formula does fit these data, and therefore how violent quantitative limitations we must impose upon our assumed new cause which is to lead to a formula closely resembling at least the relativity formula. Before making this analysis, we shall attempt to state briefly our present assumptions and our final conclusions as to the requirements which must be imposed upon this new cause.

When the system is a simple nucleus electron system, we assume that the fine structure of lines is wholly due to the relativity cause, so that we adopt as the fully adequate explanation of the character of hydrogen and ionized helium lines Sommerfeld's relativity equation :

$$\frac{\nu}{R}=\frac{(Z-\sigma)^2}{n^2}+\left[\frac{1}{4}+\frac{n-k}{k}\right]\frac{\alpha^2(Z-s)^4}{n^4}\quad .\ .\ .\quad (1)$$

We adopt further, as applicable to all radiation, the selection principle used in optics, and therefore make L_I, like $2s$, a 2_1 orbit. We also make L_{II} and L_{III}, quite like p_2 and p_1, two circular orbits which differ only in orientation.

We assume that the orbits L_I and L_{III}, like the orbits $2s$ and $2p_1$, are an ellipse (2_1) and a circle (2_2), respectively, the energies of which differ, first, because of the difference in the greater screening from the nucleus of the circular orbit than of the elliptical orbit, and, second, because of the relativity difference between these two orbits. This is equivalent to assuming that the L_I and L_{III} orbits differ in energy by the sum of the irregular doublet energy difference and the regular or relativity doublet energy difference. In optics the first difference is very large compared with the second, while in X-rays the second difference is much the larger.

With the aid of these assumptions we are able to retain the application of the relativity principle to all orbits. We now assume—and this is the point at which we try to escape from either of the two untenable horns of our dilemma—*that there is some cause acting by virtue of the difference in orientation of the two circular orbits* L_{II} *and* L_{III} *which increases the energy of the circular* L_{II} *orbit to about the amount which it would have had by virtue of relativity had it been a* 2_1 *orbit.* This cause may be magnetic in its origin, or electrostatic, or a combination of the two. The requirements imposed upon it are—

(1) that it must make the difference between L_{II} and L_{III} follow very nearly a fourth-power variation with atomic number, just as does the relativity cause ;

(2) that it must lead to nearly the same numerical constants as does the relativity equation ; and

(3) that it must make the doublet separation vary with total and azimuthal quantum numbers very closely as does the relativity equation (1).

The only advantage of this seemingly strange way out of our difficulty over that of discarding the applicability of the relativity principle altogether to electron orbits, is that we do not now demand that our new cause yield results which are so exactly in coincidence with those given by equation (1) as we should have to do if the new cause were required to fit the extraordinarily accurate data on hydrogen and ionized helium.

VI. *Imperfections in the Agreement between the Relativity Formula and Observed Doublet Separations.*

When we return now to the analysis of the doublet-separation data upon the atoms from lithium to uranium, we find, indeed, that they may be distinguished in a number of ways from the data available with a simple nucleus-electron system. Thus :

(1) They differ qualitatively in that all the elements from lithium to uranium have at least three two-quantum-number levels, viz. the $2s$, $2p_2$, $2p_1$ levels, or in X-rays the corresponding L_I, L_{II}, L_{III} levels, while in hydrogen and in helium, on the other hand, there are only the number of L levels required by the relativity theory—namely two.

This furnishes one justification for making a break in our interpretation between ionized helium and lithium.

(2) They differ quantitatively in that while equation (1) fits very exactly, according to the work of Paschen [*] and Shrum [†], the observational data on simple nucleus-electron systems for which σ and s are both zero, it is impossible to make this assertion for any other systems. Indeed, in testing the relativity equation derived from (1) by subtracting two such equations corresponding to the two azimuthal quantum numbers 1 and 2, a process which yields

$$\Delta\nu = \frac{R\alpha^2(Z-s)^4}{n^3k(k-1)}, \quad \ldots\ldots \quad (2)$$

in which in this case k = azimuthal quantum number 2, and $k-1$ = azimuthal quantum number 1, our procedure has always been simply to solve this equation for s, *which then becomes an arbitrary parameter.* For the whole series of stripped atoms, beginning with lithium, the value of s should, of course, have come out 2, since there are two screening electrons near the nucleus with all these atoms. It actually came out for stripped nitrogen 1·838, for carbon 1·858, for boron 1·884, for beryllium 1·937, and for lithium 2·019. None of these numbers is within the limit of experimental error of 2, and it will be seen that the fourth power makes a large error in $\Delta\nu$ appear as a small error in s.

We did, indeed, suggest in our preceding paper a logical explanation for the first four of these departures. Thus we assumed that the screening of the nucleus became less and less perfect as the orbit of the radiating electron came relatively closer and closer to the orbits of the screening electrons. Some such change in the perfectness of the screening with closer and closer approach to the screening electrons must take place in any case, so that the foregoing explanation must be regarded as qualitatively satisfactory. But the screening constant should then never exceed 2, no matter how far the radiating electron is removed. In the case of lithium, however, it does exceed 2 by 1 per cent., and a numerical computation shows that to cover this departure there should be an uncertainty of 7·4 per cent. in the separation of the lithium lines. Otherwise stated, their observed separation instead of being ·338 frequency units should have been ·365. The observations made by Kent [‡] on three different lines in which this doublet appears vary from ·336 to ·340, *i. e.* but one-sixth of the necessary difference. The relativity formula then, contrary to the less carefully considered opinion which we expressed in the preceding article, does not predict for this group of atoms the observed separation within what are probably *the limits of observational error.* Instead, the quantity s as we have used it is, within rather narrow limits, an arbitrary parameter with the aid of which we have forced the relativity formula into exact agreement with the observed facts.

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[*] *Ann. d. Phys.* l. p. 901 (1916).

[†] Proc. Roy. Soc. cv. p. 259 (1924).

[‡] Astrophys. Journ. xl. p. 337 (1914).

The fourth-power variation with atomic number demanded by the relativity formula does, however, fit the observed doublet separations from lithium through nitrogen very closely. How closely may be seen from the fact that, if s is fixed at 2, the $\Delta\nu$ from lithium to nitrogen is proportional to $(Z-2)^{4\cdot13}$, thus showing that whatever the cause of the separation may be, it cannot follow anything resembling a third-power law of variation with effective nuclear charge as the Heisenberg theory [*] demands.

Also that the doublet separation varies with *total quantum number* almost exactly as the relativity formula demands is shown by the fact that the screening constant for the $3p$ doublet of C_{IV} was found in Table I. of the preceding article to come out with almost exactly the same value as the screening constant for the $2p$ doublet when we inserted the relativity constants ·365 and ·108, respectively, to compute these values of s.

When the same sort of careful analysis is made for the doublet separations found in the series of stripped atoms from Na to Cl, all seven of which we have now obtained, the screening constant s is again not predicted within the limits of experimental error, even in the limiting case of the most remote orbit upon which we can make observations. Here, again, the departure is in the same direction as in the case of lithium. Thus a glance at our former Table V. shows that the most remote orbit with which we have here worked is the circular $4f$ orbit in the case of Al_{III} and Si_{IV}. For the orbits much closer than this to the nucleus the table shows, quite as we should expect, that the screening constant comes out considerably less than the $(2+8)=10$ electrons in the two inner shells. This we explain qualitatively by the same considerations advanced for the behaviour of the lithium-to-nitrogen series—namely, imperfect screening for a too close approach to the screening electrons. In the case of the elliptical p orbits this too close approach may even be an interpenetration, and thus reduce s very considerably. In S_{VI} it is reduced from 10 down to as low a value as 5·57. But in the limiting case of the very remote circular orbit $4f$ the screening constant, as computed from the observed separations with the aid of the relativity formula, came out for Al_{III} 10·341 and for Si_{IV} 10·412. A careful numerical computation of the error in $\Delta\nu$ necessary to cover this difference from 10 makes it about 50 per cent., while the observed separations, namely ·38 for Al_{III} and 1·26 for Si_{IV}, ought to be correct to within 10 per cent. at most.

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[*] *Zeits. f. Phys.* viii. p. 273 (1922).

While, then, in the case of hydrogen and ionized helium the relativity formula predicts the fine structure quantitatively to as high a degree of precision as is attainable in the experimental work, in the case of both the lithium-to-nitrogen series and the sodium-to-chlorine series, even for remote orbits which ought to obey the laws of a simple nucleus-electron system, the relativity formula predicts results which depart from the observed data by somewhat more than the observational errors contained in those data. These facts justify to some degree, at least, making a break between helium and lithium and assigning different causes to the doublet separations in hydrogen and helium from those assigned in the case of the other atoms.

It is true that in the case of these atoms also, as in the case of the lithium-to-nitrogen series, the fourth-power variation with effective nuclear charge and the third-power variation with total quantum number (equation 2), both of which are consequences of the relativity theory, fit the observed facts, as shown in Table V. (*l. c.*), extraordinarily well. So that in throwing overboard relativity as a cause we are still obliged to find an equation of the same form as the relativity equation, a certain amount of latitude being allowed merely in the fixing of its numerical constants.

There is another bit of evidence that we have just brought to light which has some bearing upon this point. We have experimentally followed the doublet separations corresponding to $3d_2-3d_1$ and $4d_2-4d_1$ throughout the whole series of stripped atoms Mg_{II}, Al_{III}, Si_{IV}, P_V, and S_{VI}, and have found that these $\Delta\nu$'s do not progress at all in the way the relativity law demands. Nevertheless, at the end of the series, *i. e.* in S_{VI}, the separation appears to be rapidly approaching the relativity value *.

The real test of the relativity formula ought to be found in its ability to yield the correct screening constant in the *limiting* cases of very remote orbits where the system becomes essentially a nucleus-electron system, for any failure in the case of close-in orbits can be thrown back upon imperfect screening. Now the 3*d* and 4*d* orbits are, in fact, remote enough to make such large departures as have appeared in the diffuse series from Mg_{II} to S_{VI} somewhat surprising and difficult to account for merely on the basis of imperfect screening. These departures, therefore, lend some support to the effort to differentiate sharply between the precise way in which hydrogen and helium follow the relativity formula and the rough way in which all other atoms behave with respect to it.

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* "The series Spectra of the Stripped Atoms of Phosphorus (P_V), Sulphur (S_{VI}), and Chlorine (Cl_{VII})," Phys. Rev. March 1924.

VII. *Consideration of Total Quantum Numbers Higher than Two—M, N, etc. Levels.*

For the sake of simplicity we have thus far confined our attention mainly to orbits of total quantum number two, *i. e.* to L orbits. From the point of view which we are here adopting, the five M levels shown in the figure, taken from Bohr and Coster*, would fit into our scheme as follows:—Levels M_I (3_1) and M_{III} (3_2) differ in energy by a difference in screening constant due to difference in shape plus a relativity difference. M_{II} is then an orbit which is like M_{III} in shape, but upon which our new hypothetical cause has operated so as to raise its energy to about the amount which it would have had by virtue of relativity had it been a 3_1 orbit. This brings the M_{II} line to essential parallelism with the M_I line. Similarly, M_{III} and M_V, which correspond to the differently shaped 3_2 and 3_3 orbits, respectively, also differ by a screening constant plus a relativity difference, while M_{IV} has been raised by the assumed new cause to such a point as to produce essential parallelism between the M_{IV} and M_{III} lines.

The fact that our postulated new cause must produce very nearly the same effect as a relativity cause, both as regards the difference between the energies of 3_1 3_2 orbits and 3_2 3_3 orbits imposes another limitation upon this cause which is almost as severe as those imposed by the necessity of varying both with effective nuclear charge and with total quantum number precisely as the relativity theory demands. In other words, the postulated cause is required to demand the same *variation* (1) with effective nuclear charge, (2) with total quantum number, and (3) with azimuthal quantum

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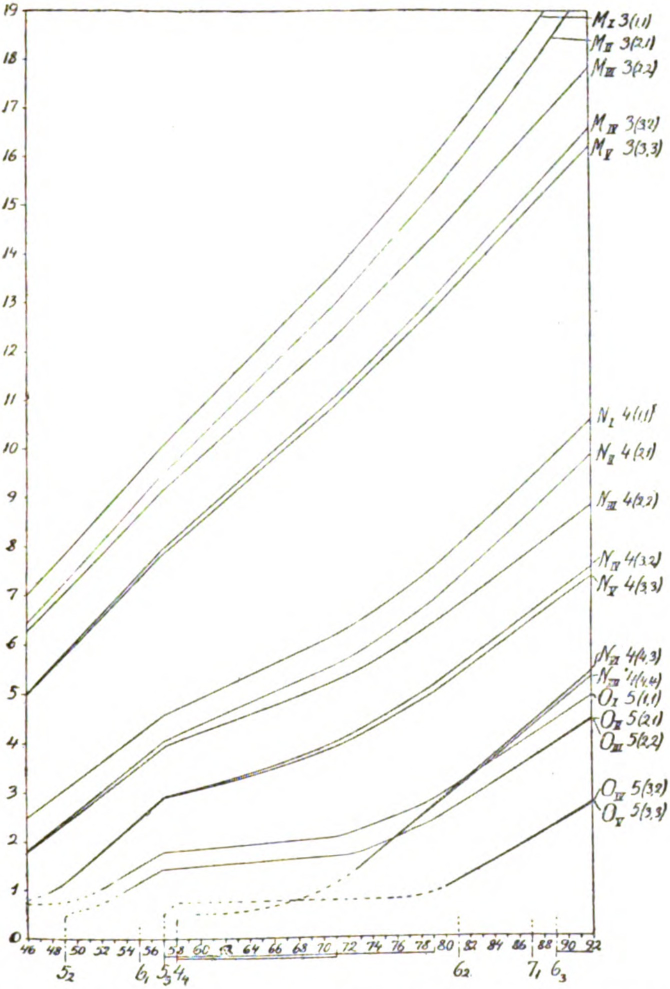
[*] *Zeit. f. Phys.* xii. p. 369 (1923).

number as is demanded by the relativity principle. But in view of the undetermined parameter *s* which is used in making the relativity formula fit the facts in the case of all optical and X-ray spectra except those of hydrogen and



ionized helium, it cannot be said that we impose anything like so exacting a quantitative condition upon our new cause as we should if we denied the relativity cause *in toto*, and hence made the new cause also take care of the spectral behaviour of hydrogen and ionized helium.

VIII. *The Bearing of the Paschen-Back Effect.*

A crucial test of the foregoing hypothesis that there is a difference in kind between the fine structure of the lines produced by a simple nucleus-electron system like atomic hydrogen and ionized helium—a structure which we have assumed to have a *real* relativity cause—and the fine structure found in the spectrum of lithium and atoms of higher atomic number—a structure which we have assumed to be due to changes in inner rather than azimuthal quantum number—should be found in a comparison of the behaviour of these different types of fine structure in magnetic fields.

Thus each of the components of the hydrogen and helium doublets ought in such a field to show the *normal* Zeeman effect, while the effect of a magnetic field upon the doublets in lithium and the like ought to be of an entirely different nature. *As a matter of fact, in weak magnetic fields this difference is known to exist in a very striking way*, the lithium doublet and the like showing the so-called anomalous Zeeman effect, while the normal Zeeman effect is shown by each of the lines of the doublet of hydrogen and ionized helium. So far as it goes, this fact lends strong support to our hypothesis.

When the magnetic fields are strong, however, it is well known that Paschen and Back * discovered that the fine structure in lithium disappears entirely, and that there is found but a single line having a normal Zeeman effect, *as is to be expected if the difference between the components of the lithium line is due to a magnetic cause*; for a sufficiently strong external field might then be expected to overcome entirely the weak magnetic influence which produces the doublet.

Upon our present theory we should not expect the Paschen-Back effect to be observable in hydrogen and ionized helium at all. In strong magnetic fields, however, so far as experimenting has now gone, the evidence seems to favour the conclusion that the Paschen-Back effect is found in hydrogen †. This weakens somewhat the force of our argument for the difference in kind between the hydrogen and lithium doublets, though the respective normal and anomalous Zeeman effects which these substances show in weak magnetic fields still makes them in one particular, at least, *distinctly* different. Further work is needed to show with certainty whether in strong fields the Paschen-Back effect is actually exhibited by hydrogen and ionized helium or not.

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* *Ann. der Physik*, xxxix. p. 897 (1912) and xl. p. 960 (1913).

† Oldenburg, *Ann. der Physik*, lxvii. p. 253 (1922). Försterling & Hansen, *Zeit. f. Phys.* xviii. p. 26 (1923).

IX. *Recapitulation.*

The evidence for a difference in kind between the fine structure of the lines of the two lightest elements, atomic hydrogen and ionized helium, and that of lithium and all the elements beyond it is so good, despite their apparent similarity in behaviour in strong magnetic fields, that we propose to attribute the doublets of atomic hydrogen and ionized helium to a true relativity cause, and to introduce a new non-relativistic cause, which, however, obeys an equation almost exactly like the relativity equation, to account for the behaviour of lithium and the elements of higher atomic number. This is the only possible way to retain both Bohr's interpenetration ideas and Sommerfeld's relativistic treatment of electron orbits; and both of them seem at present to demand retention. To find a new cause for the relativity-doublet-formula with only a little leeway in the value of the numerical constants is a problem worthy of the efforts of the theoretical physicist.

Norman Bridge Laboratory of Physics,
California Institute of Technology,
Pasadena, California.
November 24, 1924.

XCIII. *An Experimental Investigation of the Dynamical Equation of the Process of Gas-Sorption. By* D. H. Bangham, *M.A., and* W. Sever, *M.Sc. of Manchester University*[*].

THE problems presented by the phenomena of absorption (or, more generally, "sorption") and occlusion remain largely unsolved at the present time, in spite of the numerous theories which have been put forward to account for them. The theory of Langmuir[†] that the "sorbate" forms at the interface between two phases a film one (and in exceptional cases two and three) molecules in thickness has been eminently successful in cases where the molecules concerned consist of long chains of atoms; and it has been satisfactorily applied to certain types of gas-solid equilibria at very high temperatures. It does not, however, account for the well-marked phenomena of occlusion, and its application to account for all the changes taking place when a finely-divided solid is exposed to a gas is therefore conditional on the inability of the solid to occlude (*i.e.* dissolve) the gas. The essential differences between the two types of phenomena have been emphasized by McBain[*].

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[*] Communicated by Mr. D. L. Chapman, M.A., F.R.S.

[†] Langmuir, Journ. Amer. Chem. Soc. xxxviii. p. 2221 (1916); xl. p. 1361 (1918).

It has recently been shown experimentally[†] that a surface of glass, when freshly exposed to such gases as ammonia, carbon dioxide, sulphur dioxide, and nitrous oxide (at approximately constant pressure) takes up gas in accordance with the equation

$$\log s = \frac{1}{m}\log t + \text{constant},$$

where s is the quantity of gas sorbed or fixed at time t reckoned from the moment of first exposure.

This equation has been found by the authors and their collaborators to be valid in a large number of instances. It agrees well, for example, with the data given by McBain[‡] for the sorption of iodine by charcoal from solutions in benzene and toluene, and with certain of the data of Bergter[§] for the sorption of air by the same solid. It has been confirmed in these laboratories by Mr. J. B. M. Herbert for the system carborundum-ammonia gas, and by Mr. J. Stafford for the system graphite-oxygen (under low pressures). A similar type of equation has been found to govern the reverse process of desorption (in its early stages), and fair agreement with many of Richardson's[||] data for the decay of the positive ionization from hot wires obtained by applying it in the differential form.

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[*] McBain. Trans. Faraday Soc. xiv. p. 202 (1919).

[†] Bangham and Burt, Proc. Roy. Soc. A. cv. p. 481 (1924).

Loc. cit.

[§] Bergter, *Ann. der Physik* (iv.) xxxvii. p. 472 (1912).

[||] The saturation current at a given time corresponds in the notation used here to $-ds/dt$. In one case Richardson's data allow the integrated form of the equation to be tested directly. Richardson (Phil. Mag. viii. p. 405 (1904)) remarks:—

"The positive leak appears always to decay asymptotically with the time, although it does not follow an exponential law. . . . . Another way of demonstrating the same thing is to measure the total quantity Q of electricity received by the electrometer at various times. Since dQ/dt is equal to the current we have, if the simple (that is, the exponential) formula holds,

$$dQ/dt = Ae^{-kt}, \quad \text{whence} \quad Q = Q_0(1-e^{-kt}),$$

if Q_0 is the charge received by the electrometer after an infinite time has elapsed. In seeking to verify this formula curves such as those shown . . . . were obtained. It was impossible to fit these curves by so

The equation has met with no explanation, either in terms of Langmuir's theory or otherwise. The systems instanced, however, are all characterized by extreme reluctance to attain equilibrium (according to the equation none should ever be reached) and this fact, taken in conjunction with the observations that the amounts of gas taken up far exceed those necessary to form monomolecular films, points to the conclusion that the gas molecules are capable of penetrating the solid.

The present investigation is an attempt to follow the sorption process beyond the range of its obedience to the equation given above; it was thought that if it proved possible to examine the mode of approach of the sorption-value to its limit, valuable information would be obtained as to the mechanism of the change.

Carbon dioxide was chosen as the experimental gas, and a quantity of fine glass-wool, tightly packed into a tube and then carefully cleaned and dried, was used as sorbent. Before each experiment the glass was subjected to a drastic process of vacuum-heating, the containing tube being in connexion with a bulb cooled in liquid air to condense out the gases as fast as they were disengaged from the solid.

Judging from previous results with such a system, equilibrium between the carbon dioxide and glass might well have taken an impracticably long time to achieve; advantage was, however, taken of a particular tube which showed a behaviour somewhat different from the others examined *.

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simple a formula as the above; the theoretical curves become much flatter after a few minutes have elapsed, when the two coincide near the origin."

The experimental values of Q as read from the published graphs for

t=0·57, 1·32, 2·09, 3·38, 5·1, 8, 11, 18, 24, and 28 minutes,

are, respectively,

28, 35, 40, 48, 54, 60, 65, 70, 75·5, and 77 units.

The applicability to these results of a time-equation of the type considered in this paper is indicated by the approximate constancy of the quotient $Q/t^{\frac{1}{4\cdot 0}}$, which takes the respective values: 32, 33, 33, 35, 36, 36, 36, 34, 34, 32. It should be emphasized (*vide* Richardson, Proc. Roy. Soc. A lxxxix. p. 507 (1914)) that the positive carriers in such a case were not charged molecules of occluded gases, but *the ions of potassium (and sodium)*.

* The tube actually used was one of a batch prepared for the earlier experiments already described (Proc. Roy. Soc. A. cv. p. 481 (1924)), and it was filled, cleaned, and dried in exactly the same way and at the same time as the others. The single difference lay in the fact that it had been filled with carbon tetrachloride (to calibrate its dead-space) before

The results obtained with this tube confirmed the conclusion that in its initial stages the sorption is governed by the characteristic equation given above, but the constant m, instead of taking the anticipated value of ca. 12, was some two to three times smaller. Thus a far larger range of sorption values became accessible to measurement within a reasonable time, and, further, there was every hope of finding a deviation from the equation for large values of t.

The System of Measurement.

Since it was hoped to record results at short intervals over long periods of time, a somewhat elaborate apparatus was constructed, which will not be described in detail. It was of the greatest importance to keep the pressure of the carbon dioxide constant with a minimum of control on the part of the operator; and since this virtually necessitated (among other things) the immersion of the whole system in a constant temperature bath, the optical method of determining pressures was discarded, and a method was used whereby the falling of the pressure below a standard value was indicated by the making of an electrical contact. To maintain the pressure while sorption was in process, the effective volume of the system was periodically decreased by admitting mercury through an electrically controlled valve into a large glass bulb which functioned as the gas reservoir.

At the beginning of each experiment the reservoir was filled with gas to a pressure slightly lower than that at which the standard-pressure gauge had been arranged to function. Mercury was next admitted through the valve until the breaking of the electric contact indicated that the standard pressure had been reached. The pressure itself was read off a simple manometer in the gas-train, which was then cut off from the gas-reservoir by closing a tap. A volume of mercury rather greater than the deadspace volume of the sorption bulb was next admitted through the valve, and a tap connecting the gas-reservoir to the sorption bulb opened. As soon as the pressure fell to the initial value (as indicated by the making of the contact) more mercury was admitted

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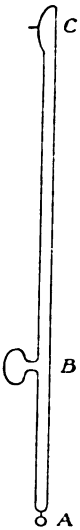
the final vacuum-heating. Carbon tetrachloride was chosen as the calibrating liquid since the use of water might have been detrimental, and it was anticipated that the non-polar nature of the tetrachloride would render it comparatively easy to remove. Apart from the different behaviour of the glass towards carbon dioxide, there was nothing to indicate that the drastic process of vacuum-heating to which the tube was subjected had not succeeded in removing the calibrating liquid completely.

to replace the gas lost by sorption. In cases where too much mercury had been admitted the excess could be run out through a tap. After the first few minutes of each experiment it was found possible, with all-night attention, to keep the pressure constant within very narrow limits indeed. Except for a short capillary tube carrying the tap between the sorption-bulb and the gas-reservoir, the entire system including the gauge was packed with ice. The quantity of mercury added up to any given time was determined by weighing periodically the bottle from which it had been taken.

The gauge consisted primarily of a mercury-filled U-tube of sufficiently wide bore to obviate significant capillary effects. Floating on the mercury in its barometer limb was a small glass bulb rigidly attached to a hinged lever-arm. This lever-arm is shown diagrammatically in the sketch (fig. 1), A being the hinge (made of platinum sealed into the glass wall of the barometer-head), and B being the float. At C a platinum wire was sealed into the lever-arm which made or broke contact with a pool of mercury contained in a bulb blown into the containing barometer-head. The barometer head itself, which was expanded to enclose the lever-arm, was connected by quill tubing to a phosphorus pentoxide tube and mercury pump, so that any gas that developed could be removed without difficulty. Since throughout each experiment the quantity of mercury in the U-tube remained fixed and its temperature constant at 0° C., the level of the mercury served to determine completely the pressure within the apparatus.

Fig. 1.



It is well known that the mercury-contact method of determining the heights of mercury columns is usually unsatisfactory though the cause of this is not fully understood. It was hoped in the present instance that the use of the lever principle (whereby errors were reduced in the ratio of AB to AC) and the fact that the contacts were maintained in a vacuum, would lead to more satisfactory results. These hopes were to some extent justified. As long as the apparatus was in constant use the indication of the standard pressure was clear and definite, and concordant results could be obtained with little trouble. When, however, in the later stages of the experiments the apparatus had been left idle for considerable periods, it was frequently very difficult afterwards to obtain concordance. In the earlier experiments an attempt was made to make the admission of mercury into the gas-reservoir automatic by causing the closing of the barometer-head circuit to operate the relay controlling the valve for admission of mercury. This method, although it had the advantage of keeping the contacts working in the absence of the operator, had finally to be given up on account of vibrational disturbances caused by traffic in the vicinity. The effect of these was to operate the valve and admit mercury long after the pressure inside the apparatus had been raised above the standard value.

Discussion of Results.

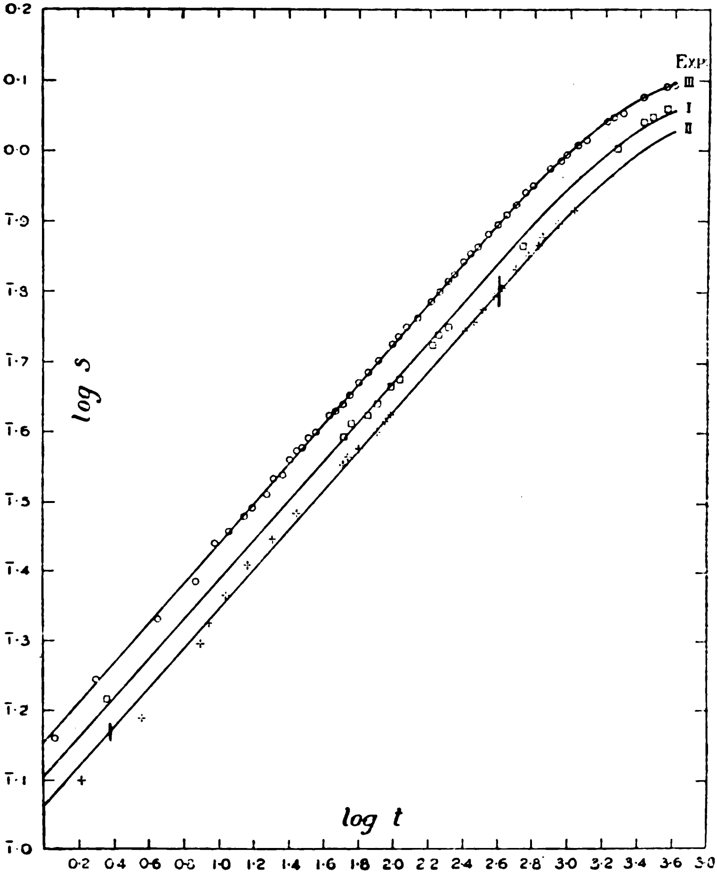
It has already been stated that the results confirm the validity of the "power" expression for the initial stages of the sorption process. This is illustrated in fig. 2 where the logs of s and t are plotted against each other. The graphs refer to three consecutive experiments all carried out at a pressure of 12·5 mm. Their linear portions cover a 5- or 6-fold range of sorption values, and it will be noticed that the lines are closely parallel.

Many of the experiments had to be discontinued on account of the erratic behaviour of the contacts following long periods of idleness. In certain cases, however, they were continued for some weeks, strictly isothermal conditions being adhered to throughout. The data for one of these protracted experiments (carried out at a pressure of 147·5 mm.) appear in the table below; in this experiment consistent data were obtained even in the later stages, as the table will show.

Apart from the extreme probability that glass is capable of dissolving small quantities of carbon dioxide, the authors have recently obtained evidence that the "power" time-law is obeyed in cases where the penetration of the solid phase by the gas can hardly be questioned. The chief interest of the present results lies, therefore, in their comparison with those to be expected on the basis of the theory of diffusion. Assuming the penetration of the solid to take place in this instance, there is every reason for concluding that "adsorption" or surface-sorption accounts for a negligible proportion only of the total effect; for the time-equation itself clearly constitutes an argument against the partition of s into two terms. In this respect the behaviour of glass as a sorbent stands in marked contrast to that of sodium chloride, for Mr. Herbert, using the latter substance, has obtained time-sorption curves which suggest that the s-value is, in their case, sharply divided into two terms, of which one only is a function of the time.

While the simplicity and general applicability of the time-sorption equation are in themselves strong arguments in favour of the view that the sorption-process is one subject to its own peculiar laws, it is nevertheless somewhat difficult to prove that the validity of such an equation in the early stages of the process necessarily involves a complete departure from the normal laws of diffusion and heat-conduction. The rate-of-sorption data obtained in the final stages of the process, on the other hand, should provide strong evidence either for or against such a departure. In discussing the question we shall merely assume that, the pressure being constant, the gas molecules at the interface are replaced from

Fig. 2.



the gas phase as fast as they diffuse into the interior of the glass.

The normal laws of diffusion would require that in the very early stages of the process (before the size and shape of the solid impose any serious limitation to the total number of gas-molecules taken up) the rate of sorption should vary as $t^{-\frac{1}{2}}$. The complete expression for the rate is given, however, by the sum of a series of exponential terms, which we may write

$$A_1 . e^{-b_1 Dt} + A_2 . e^{-b_2 Dt} + A_3 . e^{-b_3 Dt} \ldots\ldots$$

In this expression D is the unknown diffusion constant (supposed independent of the concentration), and the coefficients $b_1, b_2, b_3, \ldots\ldots$, which form a *divergent* series, are conditioned by the size and shape of the solid. Since for small values of t the sum of these terms must vary as $t^{-\frac{1}{2}}$, it is clear that in the early stages the series of exponentials converges only very slowly, and is therefore unsatisfactory as a test of agreement. For very large values of t, however, the convergence should be extremely rapid, and as s approaches closely to its limit the rate of change should be governed by the first exponential term only.

An examination of the data renders it very doubtful whether this last generalization can apply to the sorption process under consideration, the latter part of the rate-of-sorption curve being difficult to represent in terms of exponentials in t. If, on the other hand, $t^{1/m}$ is taken as the argument ($1/m$ being the constant value of $\frac{d \log s}{d \log t}$ in the early stages), it is found that a single exponential term in $t^{1/m}$ gives very fair agreement with the experimental results. Since the evaluation of the index $1/m$ from the straight portions of the $\log s/\log t$ graphs takes no cognisance of the appearance of a sorption limit, a still better agreement is obtained with a slightly higher value of this index *. In the following table experimental values of s at the times shown are compared with those calculated from the equation

$$\log_{10} \frac{3{\cdot}07}{3{\cdot}07 - s} = 0{\cdot}0501 t^{0{\cdot}364}.$$

In this equation 3·07 c.c. (N.T.P.) is the limiting value of s for $t = \infty$. This quantity of carbon dioxide, concentrated as a dense film at the external surface of the glass fibres, would have formed a layer of about three molecules' thickness. In their experiments with glass fibres and carbon dioxide at

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* It is clear, from the type of equation considered, that the evaluation of this index from the $\log s/\log t$ graphs is unsatisfactory.

TABLE I.

Experimental pressure = 147·5 mms.

Time	c.c. at N.T.P.		Diff.	Time	c.c. at N.T.P.		Diff.
(mins.).	*s* obs.	*s* calc.	1=0·01c.c.	(mins.).	*s* obs.	*s* calc.	1=0·01c.c.
4·50 ...	0·55	0·55	—	336 ...	1·88	1·90	—2
6·08 ...	0·65	0·62	+3	379 ...	1·94	1·95	—1
7·50 ...	0·67	0·66	+1	436 ...	2·00	2·00	—
10·1 ...	0·75	0·73	+2	474 ...	2·03	2·03	—
13·0 ...	0·80	0·78	+2	514 ...	2·06	2·07	−1
16·8 ...	0·86	0·85	+1	549 ...	2·10	2·10	—
20·3 ...	0·88	0·90	−2	579 ...	2·13	2·12	+1
24·2 ...	0·95	0·95	—	619 ...	2·15	2·14	+1
28·6 ...	0·97	1·00	−3	794 ...	2·27	2·24	+3
39·7 ...	1·10	1·10	—	1,115 ...	2·41	2·38	+3
48·3 ...	1·12	1·16	−4	1,400 ...	2·49	2·46	+3
53·3 ...	1·20	1·20	—	2,340 ...	2·62	2·63	−1
65·9 ..	1·26	1·26	—	2,554 ...	2·64	2·66	−2
70·1 ...	1·29	1·29	—	3,980 ...	2·78	2·78	—
73·8 ...	1·30	1·31	−1	5,560 ..	2·84	2·86	−2
98·0 ...	1·41	1·41	—	6,640 ...	2·85	2·89	−4
132	1·51	1·52	−1	10,000 ...	2·96	2·95	+1
164	1·59	1·60	−1	12,730 ...	2·97	2·99	−2
187	1·66	1·66	—	16,700 ...	3·01	3·01	—
209	1·71	1·70	+1	19,630 ...	3·02	3·02	—
*242	1·76	1·76	—	22,540 ...	3·04	3·03	+1
266	1·79	1·80	−1	26,900 ...	3·04	3·04	—
279	1·82	1·82	—	37,150 ...	3·10	3·05	+5
300	1·85	1·84	+1	46,550 ...	3·05	3·06	−1
318	1·87	1·87	—				

* At this stage a minute quantity of mercury was spilt; its amount was, however, so small that it could be estimated (by eye) almost to within the normal experimental error.

about the same pressures, Evans and George † found the sorption to correspond to a a layer of 5·5 molecular diameters. The difference is undoubtedly due to differences in the quality and treatment of the glass, and in particular to the presence in the solid (as part of its structure) of different amounts of water in the two cases. Considered by themselves these sorption values do not represent an overwhelming excess over those required by Langmuir's theory, especially if a furrowed surface be ascribed to the fibres of glass. Far greater sorption values have, however, been recorded for other gases ‡, and have been found to be controlled by laws similar to those here considered §.

Interesting comparisons can be drawn between the results recorded here and those of the older experiments of Bangham and Burt, since the same glass was used in the two cases, and it was submitted to the same vacuum-heat treatment. The fact that the course of the sorption was so different in the two cases is by no means inconsistent with the view that the same equilibrium value might ultimately have been reached at the same pressure. If this assumption be made calculation shows that after 48 hours' exposure to carbon dioxide at 147 mms. pressure* the glass of Bangham and Burt was less than 50 per cent. saturated, in spite of the fact that their early sorption values were considerably greater than those recorded in the table. Moreover, even supposing the equation $s=kt^{1.12}$ (which was found to govern the process during the first 48 hours) to have continued valid throughout, the equilibrium value would have been closely approached only after 2–3 years.

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† Evans and George, Proc. Roy. Soc. A. ciii. p. 190 (1923).

‡ Evans and George, *loc cit.*

§ Bangham and Burt, *loc. cit.*

Summary and Conclusions.

1. The equation $d \log s/d \log t = \text{constant}\left(\frac{1}{m}\right)$ for the early stages of the process of sorption on glass surfaces is confirmed, the experiments showing it to be valid over a range of sorption values of ca. 6 : 1. The value of $1/m$ is shown to be highly susceptible to changes in the past history of the glass, and probably to the presence of minute amounts of impurity.

2. Time-sorption data beyond the range of obedience to the above equation have been obtained, and are shown to be closely represented by a formula of the type

$$\log \frac{\sigma}{\sigma - s} = kt^{1/m},$$

where σ is the limiting value of s as t approaches infinity.

This approximates to the former equation for small values of s and t.

3. Equations of this type appear to be applicable in a large number of dynamical processes involving the passage of matter from the gaseous to the solid state, and *vice versa*. While there are reasons for believing that the phenomena occurring are not restricted to the boundary layer, but involve a transport of matter through the solid medium, strong evidence is given that the laws governing the changes concerned are not those of ordinary diffusion.

The authors' thanks are due to Dr. Burt and Mr. Angus Core for their continued interest in this work, and for their many helpful suggestions.

We acknowledge also the receipt of a grant from the Brunner Mond Research Fund, which has materially assisted in defraying the expenses of the investigation.

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* No actual experiment was carried out at this pressure, but the data recorded are sufficiently full to allow the interpolation to be made without difficulty.

XCIV. *The Crystal Structure of Magnesium Fluoride.*

By H. E. Buckley, *M.Sc., Assistant Lecturer in Crystallography, and* W. S. Vernon, *M.Sc., Assistant Lecturer in Physics, Manchester University* *.

Introductory.

MAGNESIUM fluoride (MgF_2) is found in nature as the mineral selläite. It is described by Groth † as crystallizing in the dipyramidal class of the tetragonal system with $a : c = 1 : 0{\cdot}6596$. The chemically prepared magnesium fluoride is a finely-divided powder consisting of minute crystals which belong to the same class of symmetry as the natural mineral.

Determinations of the density by different authorities show rather large discrepancies. E. G. Cossa gives 2·857, Struver 2·972, and Sella 3·153. The value found by the authors as the result of X-ray measurement (3·11) lies between the two latter measurements.

Experimental.

The powder method of crystal analysis was used in this investigation. A cylindrical camera was used of 2·5 cm. radius, designed on the lines of the camera described by Bradley ‡. The source of X-rays was a Siegbahn tube with a copper anticathode.

With a tube current of 20 milliamperes, satisfactory results were obtained with an exposure of one hour. The magnesium fluoride used was the purified chemical precipitate, and this was mounted on a hair with fish-glue.

The first film which was taken in this manner was found to have on it lines which were very broad and diffused, indicating that the particular powder was sub-microscopically fine. It was heated to redness for several hours in order to enable the minute particles to coalesce, and the mass was then uniformly ground up in an agate mortar. This treatment was found to be successful, all the lines on subsequent films appearing sharp and bright. An additional photograph was also taken, using the apparatus described by Bradley (*loc. cit.*), the result of this exposure being used to corroborate the results obtained by us. The films were measured by means of a travelling-stage microscope, and the results, averaged out for eight films, are included in the first column of Table I.

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* Communicated by Prof. W. L. Bragg, F.R.S.

† Groth, *Chemische Krystallographie*, i. p. 205.

‡ Bradley, A. J., "Arsenic," Phil. Mag. xlvii. p. 657 (1923).

TABLE I., with Copper (Kα) Radiation.

Average Distance in mm. from centre.	Angle of Reflexion.	Spacings in Å.U.		*h k l.*	Obs. order of Intensity.	Calc. order of Intensity.
		Obs.	Calc.			
—	—	—	4·654	100	—	—
11·95	13° 27′	3·311	3·300	110	4	4
—	—	—	3·076	001	—	—
15·45	17 26	2·568	2·567	011	26	28
—	—	—	2·327	200	—	28
17·70	19 56	2·257	2·249	111	2	2
19·28	21 43	2·080	2·085	210	5	6
—	—	—	1·858	201	—	—
23·50	26 28	1·727	1·727	211	2	2
24·82	27 58	1·644	1·650	220	8	10
—	—	—	1·551	300	—	—
26·64	30 0½	1·539	1·538	002	9	10
28·10	31 38½	1·469	1·472	310	28	28
—	—	—	1·461	102	—	—
28·45	32 4Z	1·450	1·450	221	19	19
29·97	33 47½	1·389	1·396	301	1	1
			1·392	112		
31·47	35 27½	1·329	1·329	311	19	20
32·75	36 54	1·283	1·288	320	24	24
			1·283	022		
34·38	38 44	1·230	1·235	212	10	10
35·80	40 20½	1·192	1·192	321	26	28
36·83	41 28	1·162	1·164	400	22	23
38·42	43 17	1·123	1·127	410	5	5
			1·124	222		
39·64	44 39	1·095	1·099	330	13	13
—	—	—	1·092	302	—	—
—	—	—	1·088	401	—	—
41·30	46 30	1·061	1·060	411	13	16
—	—	—	1·051	132	—	—
42·40	47 45	1·040	1·042	420	17	21
—	—	—	1·035	331	—	—
—	—	—	1·029	003	—	—
44·80	50 28	0·998	1·001	103	28	28
45·63	51 24	0·985	0·988	421	15	13
			0·988	322		
46·23	52 4	0·976	0·978	113	24	16
—	—	—	0·939	303	—	—
49·91	56 14	0·929	0·931	500	19	22
			0·931	430		
			0·924	402		
50·67	57 4	0·917	0·920	123	15	15
51·34	57 50	0·909	0·912	412	10	8
			0·909	510		
			0·892	332		
53·06	59 45	0·891	0·891	431	7	6
			0·891	051		
—	—	—	0·875	511	28	24
—	—	—	0·874	223	—	27
56·37	63 30	0·860	0·860	520	18	18
			0·863	422		
57·51	64 46	0·854	0·855	033	10	9
58·65	66 5	0·842	0·842	133	22	24
					Σ (53 planes) = 41	

The Unit Cell.

The spacings corresponding to these lines are found in the third column of Table I.

Using the density = 3·11 estimated above, and with *two molecules* of MgF_2 to the unit cell, a series of spacings may be calculated which show a close correspondence (column 4, Table I.) with the observed values.

The dimensions of a unit cell containing two molecules of MgF_2 are as follows :—

“a” = 4·654 Å (calc.) ; 4·660 Å (obs.).
“c” = 3·076 „ ; 3·078 „
$a : c = 1 : 0·6596$ „ ; 1 : 0·660 „

In the fifth column of Table I. are found the (indices of the) planes associated with each line on the film. In the sixth column the lines are grouped according to their observed intensities. Thus the strongest line is labelled 1, the remainder go in descending order of magnitude to 28, and those planes of which the intensities lie below the “ 28 ” value are not sufficiently strong to be observed or do not give any reflexion at all.

Position of the Atoms in the Structure.

A study of the lines given in Table I. shows that with lines of the type $(0kl)$, where $(k+l)$ is odd, the spacings are halved. This is characteristic of two space-groups, viz. D_{4h}^{14} and C_{4v}^{4}. In both cases, since there are only two magnesium atoms, the latter must be situated on a centred tetragonal prism whose coordinates are (000) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. There are four fluorine atoms, and these in D_{4h}^{14} are placed at points with coordinates

$$\tfrac{3}{4}-p,\ \tfrac{3}{4}-p,\ 0;\ \ \tfrac{1}{4}+p,\ \tfrac{3}{4}-p,\ 0;\ \ \tfrac{1}{4}-p,\ \tfrac{1}{4}-p,\ \tfrac{1}{2};\ \ \tfrac{3}{4}+p,\ \tfrac{3}{4}+p,\ \tfrac{1}{2}\ \ \ldots \qquad (A)$$

or

$$\tfrac{3}{4}-p,\ \tfrac{3}{4}-p,\ \tfrac{1}{4};\ \ \tfrac{1}{4}+p,\ \tfrac{3}{4}-p,\ \tfrac{1}{4};\ \ \tfrac{1}{4}-p,\ \tfrac{1}{4}-p,\ \tfrac{3}{4};\ \ \tfrac{3}{4}+p,\ \tfrac{3}{4}+p,\ \tfrac{3}{4},\ \ldots \qquad (B)$$

where “p” may assume positive or negative values. In C_{4v}^{4} the four fluorine atoms are to be found at points whose coordinates are

$$\tfrac{3}{4}-p,\ \tfrac{3}{4}-p,\ q;\ \ \tfrac{1}{4}+p,\ \tfrac{3}{4}-p,\ q;\ \ \tfrac{1}{4}-p,\ \tfrac{1}{4}-p,\ 0-q;\ \ \tfrac{3}{4}+p,\ \tfrac{3}{4}+p,\ 0-q,$$

where again “p” may assume positive or negative values. In D_{4h}^{14} (001) and (003) should be absent, while in C_{4v}^{4} these lines should be present. Neither is to be found on the films. It would also appear, from the occurrence of a strong (002) line, that the two sorts of atoms lie in the same plane, in which case the arrangement C_{4v}^{4} will assume the higher symmetry of D_{4h}^{14}. The latter arrangement therefore appears more than likely. Finally it will be shown that for a particular value of "p," in D_{4h}^{14} marshalling, there is a good agreement between calculated and observed intensities.

In D_{4h}^{14} the F atoms may be in the same plane as the Mg atoms, or they may interlace these. A choice between these two possible types is therefore necessary, and recourse must be made to a comparison of calculated and observed orders of intensity for the different lines. In order to evaluate the intensities of reflexion given by planes with different arrangements of atoms, certain assumptions as to the relative scattering power of magnesium and fluorine atoms are necessary. The rate of falling off of intensity with increase in the glancing angle must also be considered. The latter is assumed to be proportional to the inverse square of the sine of the angle, and, as a fair approximation, the relative scattering power of Mg and F was taken as 10 : 10, *i.e.* the two kinds of atoms are practically of equal weight. As a preliminary test, the two possible arrangements in which $p=0$, viz. $\frac{3}{4}, \frac{3}{4}, 0$; $\frac{1}{4}, \frac{3}{4}, 0$; $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$; $\frac{3}{4}, \frac{3}{4}, \frac{1}{2}$ and $\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$; $\frac{1}{4}, \frac{3}{4}, \frac{1}{4}$; $\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$; $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$, were tried. Neither of these gives satisfactory orders of intensities for the lines. In both cases all calculated intensities are found to be identical with each other except those for lines of the type (*2h*. *2k*. 2), *e.g.* 002, 022, 222, 042, 242, and for the latter lines the arrangement in which Mg and F atoms are in one plane gives fair results when compared with the observed orders of intensity for these lines, while the alternative, in which Mg atoms are interleaved with F atoms, gives totally incorrect orders. This is confirmed by the previous observation regarding the strength of the (002) line. There appears, therefore, little doubt that the Mg and F atoms do lie in one plane, and that the arrangement marked "A" of D_{4h}^{14} is the correct one. There is a displacement "p" *to* or *from* a Mg atom parallel to the (110) plane with coordinates, if displaced in the latter direction, of

$$\tfrac{3}{4}-p,\ \tfrac{3}{4}-p,\ 0\ ;\ \tfrac{1}{4}+p,\ \tfrac{3}{4}-p,\ 0\ ;\ \tfrac{1}{4}-p,\ \tfrac{1}{4}-p,\ \tfrac{1}{2}\ ;$$
$$\tfrac{3}{4}+p,\ \tfrac{3}{4}+p,\ \tfrac{1}{2}.$$

If the displacement be *towards* an Mg atom, "p" will then have an opposite sign to that given. There will then be an extraordinarily high value for the (110) spectrum, whereas the latter was not observed to be as strong as (112+301) or (111) or (211) spectra. Moreover, it will give a very small value for the distance Mg–F. The displacement is therefore most likely in a direction *away* from an Mg atom.

Calculations were made of intensities, on this arrangement, of the following lines:—110, 011, 200, 111, 210, 211, 112+301, 220, 222+410, 400, 330, 033, 332+051+431 (eighteen in all). Values of the parameter were taken for every five degrees from 100° to 130°. The resulting intensities were arranged in descending order of magnitude and compared with the observed order for these lines. The differences in order for each line were noted, and a sum (Σ) of these for each value of "p" taken, as shown in Table II.

TABLE II. (18 planes).

$p \times 360° =$ 130°	125°	120°	115°	110°	105°	100°
$\Sigma =$ 30	30	23	19	19	24	31

There is a minimum error in the neighbourhood of 110°–115°. This region was explored more thoroughly, every possible plane from (100) to (133), fifty three in all, being used. The results are given in Table III.

TABLE III. (53 planes).

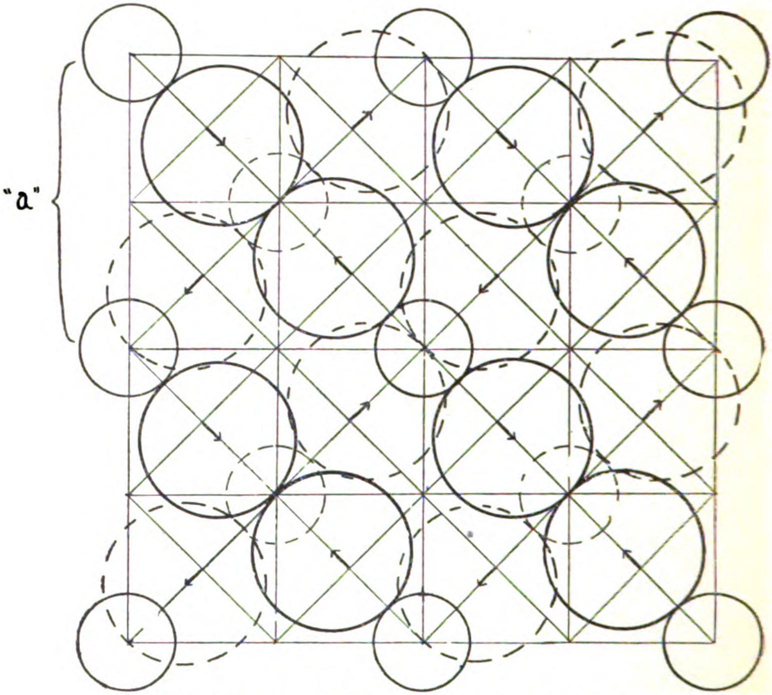
$p \times 360 =$ 115°	114°	113°	112°	111°	110°
$\Sigma =$ 53	52	41	53	61	72

The best value of "p," therefore, is in the region of $\frac{113}{360}$, where the average error per line is about ¾ of 1 unit. The complete order of calculated intensities for this value of "p" is given in the last column of Table I.

Description of Structures.

Magnesium fluoride crystallizes on an arrangement possessing the symmetry of space-group D_{4h}^{14}. "Mg" atoms are located on a centred-tetragonal space-lattice with a unit interval of "a" = 4·660 Å and "c" = 3·078 Å, while the "F" atoms lie in the same 001 planes as their "Mg" neighbours and are associated with them, grouped in pairs about each (fig. 1). The distance apart of Mg to F is 2·07 Å. This is in substantial agreement with the value obtained by adding Bragg's later radii for these elements, viz. 2·08 Å. It is interesting to note that the structure is similar in type to rutile (TiO_2), in spite of the apparent chemical differences in both atoms and valencies involved. That this similarity is not merely fortuitous is shown by a glance at Table IV., where a comparison of the crystallographic properties of rutile, MgF_2, and cassiterite is given. The agreement is very striking for substances so apparently dissimilar.

Fig. 1.



Larger circles denote fluorine atoms, smaller circles magnesium atoms.

TABLE IV.

		Rutile.	MgF_2	Cassiterite.
$a:c$.		1 : 0·644	1 : 0·660	1 : 0·672
Cleavage.		100 & 110 good.	100 & 110 good.	100 & 110 good.
Mol. per unit cell.		2	2	2
Dimensions of unit cell	$a =$	4·58 Å.	4·66 Å.	4·67 Å.
	$c =$	2·92 ,,	3·08 ,,	3·14 ,,
Distance RR′.		TiO = 1·99 Å.	MgF = 2·07 Å.	SnO = 2·08 Å

The constants of MgF_2 appear to be intermediate in character between those of rutile and cassiterite.

Summary.

Magnesium fluoride (MgF_2) is found to crystallize on a structure possessing the symmetry of D_{4h}^{14}. The unit cell is a tetragonal prism with $a=4{\cdot}660$ Å, $c=3{\cdot}078$ Å, and $a:c=1:0{\cdot}660$. The distance of closest approach of Mg to F is 2·07 Å, agreeing with a calculated value of 2·08 Å. The structure is similar to that of rutile (TiO_2), with which it possesses several properties in common.

The authors desire to take this opportunity of expressing their gratitude to Professor W. L. Bragg for his help and advice, also to Mr. R. W. James and Dr. A. J. Bradley for assistance rendered during the course of the research.

XCV. *The Arc Spectra of Silver and Copper.*

By A. G. Shenstone, Ph.D.*

[Plate IX.]

THE spectrum obtained from the ordinary copper or silver arc in air contains a great many spark lines often imperfectly distinguishable from the true arc lines. As a first step in the disentangling of the series relationships of these metals, experiments have been carried out to separate completely the lines due to the ionized and unionized atoms. A preliminary report appeared in 'Nature' of October 4, 1924 (vol. cxiv. p. 501).

If a sufficiently high density of metal vapour can be supplied, arcs can be maintained in these metals at voltages as low as six volts. Even under these conditions, however, it cannot be known with certainty that all spark lines have been eliminated owing to the presence of cumulative ionization. But if the vapour is bombarded with low velocity electrons and no arc is allowed to form, there should be emission of lines due to the unionized atom only. This can be accomplished by means of the three electrode arrangement devised by Foote, Meggers, and Mohler †, in which the electrons from a hot filament are accelerated through a grid

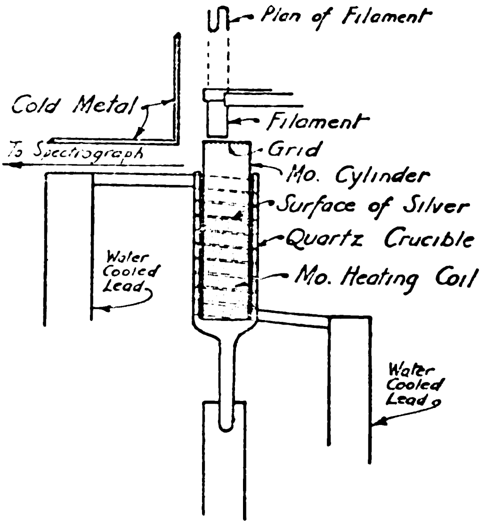
* Communicated by the Author.

† Phil. Mag. xlii. p. 1002-15 (1921).

into a force free space. The apparatus used for silver is shown in fig. 1.

The 15 mil tungsten filament was placed very close to the grid at the top of the crucible, and the electrons were accelerated by a suitable potential, usually about 10 volts, applied between the filament and the grid. The radiation resulting from the bombardment of the silver atoms in the mouth of the crucible was photographed by means of a small quartz spectrograph. The apparatus was enclosed in a water-cooled, vacuum-tight metal container, provided with quartz windows, and the rate at which the windows silvered over was reduced by a flow of hydrogen at about ·01 mm. pressure.

Fig. 1.



Under such conditions a maximum exposure of about three-quarters of an hour could be made.

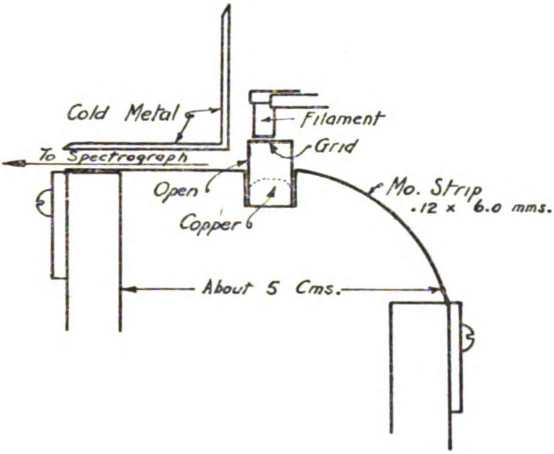
Using either copper or silver, it is not difficult with this apparatus to obtain the "single-line" spectrum by applying a sufficiently low voltage. To obtain the complete arc spectrum of silver a potential of nine to ten volts was employed. In agreement with the analysis of the silver spectrum as given by Fowler *, only one pair of lines (λ 2061·19 and λ 2069·85) was obtained below the first pair of the principal series (λ 3280 66 and λ 3382·86). The former pair was measured as accurately as possible on plates given by a perfectly adjusted small Hilger quartz spectrograph, and they

* Fowler, "Report on Series in Line Spectra," p. 111 (1922).

were found to agree much more closely with the calculated values than with the measurements of Piña [*]. There is little doubt from these experiments that the accepted energy levels of the silver atom are correct.

For the equivalent experiment with copper another form of furnace was found more suitable (fig. 2).

Fig. 2.



The crucible in this case was a cylinder of molybdenum strip having an opening toward the window of the apparatus and a grid at the top. A heating current of 70 amperes, through the supporting molybdenum strip, produced copper vapour at a sufficient rate for the experiment. As in the work with silver, a 15 mil filament was used, giving, at 10 volts, an emission of about 6 to 10 m.a.

The lines [†] of the copper spectrum photographed under these conditions are given below, together with additional lines (marked with an asterisk) which appear in the arc at about 8 volts and ½ amp. ? The intensities are estimated roughly from the best plate obtained of the low-voltage arc spectrum. The spectrum was obtained on a Schumann plate (Table I.).

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[*] Fowler, "Report on Series in Line Spectra," p. 111 (1922).

[†] Wave-lengths in this paper, except where noted, were obtained from Kayser und Konen, *Handbuch der Spectroscopie*, vii. pp. 334–352.

TABLE I.

	Intensities.	
	Hasbach.	8 Volt.
2024·33 *		1
† 2138·44 *	1*u*	1
2165·06	1*u*	4
2169·49 *	2*u*	0
2171·75 *	1*u*	0
2178·91	1*u*	4
2181·68	1*u*	4
2199·65 *	6R	2
2214·56 *	6R	3
2215·65 *	4R	2
2225·665	2R	3
2227·74 *	6R	2
2230·071	6R	3
2236·22 *	1*u*	0
2238·43 *	2*u*	1
2244·240 *	2	1
2260·493 *	4	0
2263·09 *	6R	1
2293·832 *	8R	3
2392·629 *	8*r*	1
2441·625	6	2
2492·142	8	3
2618·381	10*r*	5
2766·388	8	4
2824·375	8	4
2882·937	4	4
2961·177	6	5
2997·363 *	4 }	1
2998·384 *	2 }	
3010·840	5	2
3036·105	6	5
3063·416	6	5
3073·803 *	4	1
3093·993 *	6	2
3156·623 *	3	0
3194·103 *	6	1
3208·236 *	4	1
3247·550	10R	20
3273·967	10R	20

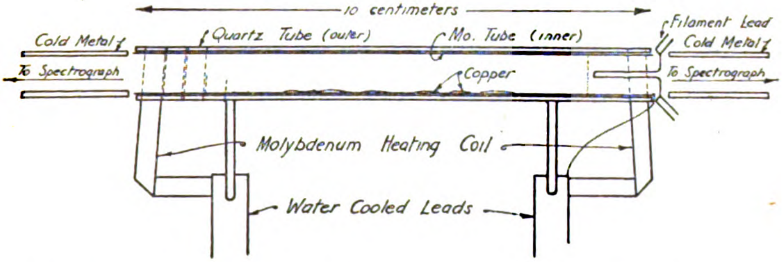
(It will be noted that this list includes λ 2178·91, which was given incorrectly in my letter to 'Nature' as λ 2179·39).

† Simeon and Dreblow ('Nature,' cxiv. p. 751, 1924) give 2138·49.

The wave-length given for the line λ 2024·33 is the value obtained from combinations. This line was measured carefully on five plates of the ordinary arc, using a perfectly focussed small spectrograph, and the following values were obtained :—2024·30, ·35, ·30, ·36, giving an average of 2024·33. The value given by Piña is λ 2024·05. The line is quite strong in the low voltage arc and certainly has no accompanying arc-line of comparable intensity in the neighbourhood.

If the scheme of the copper arc spectrum is as given by Fowler, all lines in the region below λ 3148, the limit of the subordinate series, should be produced by transitions to the levels 1*s*, X, or levels of the same nature of X. Observations of absorption would differentiate between these alternatives. An apparatus (fig. 3) was therefore set up to determine which of these many lines were absorbed by copper vapour.

Fig. 3.



The apparatus consisted of a molybdenum tube within a quartz tube heated by means of a molybdenum coil. Near one end was a grid and in that end an arc was struck from a hot filament to the inner tube. The whole apparatus was enclosed as before. Simultaneous photographs of the spectrum were taken by two small quartz spectrographs placed opposite the two ends of the tube. A comparison of the two spectra shows that the following lines were definitely absorbed by the column of copper vapour :—

λ 2165·06
2225·665
2244·240
2441·625
2492·142.

The two lines λ 2181·68 and λ 2024·33 were not quite certainly absorbed, and the line λ 2178·91 was not sufficiently resolved from 2179·37. But all of these are certainly $1s-p$ lines, as will be seen from combinations. By a slightly different method the absorption of λ3247·550 and λ3273·967 was shown *.

The level called X by Dunz is known from Zeeman data to be an md_2 level †. Dr. Ruark, of the Bureau of Standards, Washington, suggested the value of the other level of this pair md_1 as 51105, which has been altered to 51105·5 to fit the combinations which have been calculated. Using this value for md_1, $md_2=49062·6$ and $1s=62308$, the combinations given in Table II. are found.

In a footnote to his paper "Linienspektren und Atombau" (*Ann. d. Phys.* lxxi. s. 268, 1923) Bohr mentions that Werner has found the term md_1 and a number of combinations with it. No values are given.

In Table II. the wave-lengths and intensities are, where possible, Hasbach's. In the region of long wave-lengths the measurements of Meggers and Aretz have been used.

It will be seen from Table II. that the two pairs of levels np_a and np_b, np_c and np_d have abnormally large separations 829·7 and 371·6. They are also reversed from the usual order, *i. e.*, the larger term has the inner quantum number 2. If these two pairs are successive members of a series of p levels, it is strange that there are not present in the spectrum any lines resulting from the lower members of the same series. Moreover, the relative intensities of the combination lines are not at all regular. Ruark, Foote, and Mohler have found inverted doublet terms in helium, but in that case the intensities of the p_d lines were such as would be expected from the inner quantum numbers ‡.

Of the pair of levels np_e and np_f, the smaller, np_f, has the inner quantum number 2, and they may, therefore, be the normal $3p_2$ and $3p_1$. This conclusion is given weight by the fact that one plate has been obtained on which the only lines appearing below the principal pair are λ 2181 and λ 2179, although usually in the low voltage arc this is not the strongest pair. Moreover, it is seen that the intensities of these two lines are relatively much greater in the low voltage arc than in the ordinary arc in air. The remaining two levels, np_g and np_h, are very difficult to fit into a doublet system. np_h combines strongly with md_1 and md_2 and has, therefore, inner quantum number 2. The line $1s-np$ at λ 2024·33 is apparently the only arc line in a large region of the spectrum. No evidence is available as to the fineness

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* W. Grotrian, *Zeits. f. Physik*, xviii. 3–4, pp. 169–182 (1923).

† Paschen-Goetze, 'Seriengesetze der Linienspektren,' foot of p. 68.

‡ Ruark, Foote, and Mohler, Opt. Soc. Am. Journ. vol. viii. p. 17, Jan. 1924.

TABLE II.

	ν (calc.).	λ.	ν (obs.).
	$2p_2=31772\cdot8$.	$2p_1=31524\cdot4$.	
$1s-2p_2$	30535·2	3273·97 (10R)	30535·2
md_2-2p_2	17289·8	5782·16 (8)	17289·8
$1s-2p_1$	30783·6	3247·55 (10R)	30783·6
md_1-2p_1	19581·1	5105·55 (8*u*)	19581·1
md_2-2p_1	17538·2	5700·25 (6)	17538·2
	$np_a=22194\cdot0$.	$np_b=21364\cdot3$.	
$1s-np_a$	40114·0	2492·142 (8)	40114·0
md_1-np_a	28911·5	3457·856 (3)	28911·4
md_2-np_a	26868·6	3720·770 (2)	26868·6
$1s-np_b$	40943·7	2441·625 (6)	40943·9
md_2-np_b	27698·3	3609·300 (2)	27698·3
	$np_c=17763\cdot9$.	$np_d=17392\cdot3$.	
$1s-np_c$	44544·1	2244·240 (2)	44544·7
md_1-np_c	33341·6	2998·384 (2)	33341·6
md_2-np_c	31298·7	3194·103 (6)	31298·7
$1s-np_d$	44915·7	2225·665 (2R)	44916·4
md_2-np_d	31670·3	3156·623 (3)	31670·3
	$np_e=16487\cdot2$.	$np_f=16428\cdot8$.	
$1s-np_e$	45820·8	2181·68 (1*u*)	45821·7
md_2-np_e	32575·4	3068·912 (2)	32575·4
$1s-np_f$	45879·2	2178·91 (1*u*)	45880·2
md_1-np_f	34676·7	2882·937 (4)	34676·7
md_2-np_f	32633·8	3063·416 (6)	32633·8
	$np_g=16135\cdot2$.	$np_h=12925\cdot0$.	
$1s-np_g$	46172·8	2165·06 (1*u*)	46173·6
md_1-np_g	34970·3	2858·737 (2)	34970·2
md_2-np_g	32927·4	3036·105 (6)	32927·4
$1s-np_h$	49383·0	2024·33 (?)	49383·0
md_1-np_h	38180·5	2618·381	38180·2
md_2-np_h	36137·6	2766·388 (8)	36137·6

of this line. The level np_g combines strongly with md_2. In the ordinary arc it also combines with md_1, giving λ 2858·74, but no line at this point is obtained in the low-voltage arc, indicating that this level may have inner quantum number 1. The line $1s—np_g$ λ 2165·06 is a very fine line in the spark spectrum under high dispersion and can hardly be double. In the arc spectrum it shows a single fine reversal.

In the following table are found calculated energy levels which may be further p-terms:—

TABLE III.

	ν (calc.).	λ.	ν (obs.).
		Q=7280·3.	
md_1—Q	43825·2	2281·07 (2)*	43825·4
md_2—Q	41782·3	2392·629 (8*r*)	41782·3
1*s*—Q	55027·7	1817·3 (1)	55026·7
		M=5964·3.	
md_1—M	45141·2	2214·56 (6R)	45141·6
md_2—M	43098·3	2319·561 (4)	43098·3
1*s*—M	56343·7	1774·4 (2)	56357·1
2*s*—M	13206·8	7570·09 (5)	13206·3
		K=4888·9.	
md_2—K	44173·7	2263·09 (6R)	44173·7
1*s*—K	57419·1	1741·6 (5)	57418·5
2*s*—K	14282·2	7000·02 (1*u*)	14281·7
		J=4358·4.	
md_1—J	46747·1	2138·49 (1*u*) †	46747·1
md_2—J	44704·2	2236·22 (1*u*)	44704·3
1*s*—J	57949·6	1725·9 (3)	57940·8
2*s*—J	14812·7	6749·29 (2*u*)	14812·3
		N=4188·2.	
md_1—N	46917·3	2130·700 (1)	46918·0
md_2—N	44874·4	2227·74 (6R)	44874·4
2*s*—N	14982·9	6672·23 (3)	14983·4
		R=3943·2.	
md_1—R	47162·3	2119·80 (0)*	47159·4
md_2—R	45119·4	2215·65 (4R)	45119·4
2*s*—R	15227·9	6565·54 (3*u*)	15226·8

* Wave-lengths due to Piña.
† Simeon and Dreblow (*loc. cit.*).

Of these, M and J may possibly be $5p$ and $6p$, but in that case no line occurs corresponding to $1s—4p$.

Further possible levels are given in the following table :—

TABLE IV.

	ν (calc.).	λ.	ν (obs.).
A = 18581·9.			
md_1—A	32523·6	3073·803 (4)	32523·6
md_2—A	30480·7	3279·823 (3)	30480·7
B = 17901·8.			
md_1—B	33203·7	3010·840 (5)	33203·7
md_2—B	31160·8	3208·236 (4)	31160·8
E = 15709·8.			
md_1—E	35395·7	2824·375 (8)	35395·7
md_2—E	33352·8	2997·363 (4)	33353·0
$2p_2$—E	16063·0	6223·66 (3*u*)	16063·3
F = 7523·8.			
md_1—F	43581·7	2293·832 (8R)	43581·7
md_2—F	41538·8	2406·661 (6)	41538·7

The lack of further combinations with these terms makes their interpretation very doubtful at present. It may be that here, and also in some cases in Table III., we are dealing with p' and d' terms: in particular A and B are probably d' terms, although the intensities are not such as would be expected. Zeeman types of some of the important lines should settle such points.

In an attempt to find confirming combination lines, the differences of all the terms, old and new, of the copper spectrum have been taken, with very little result. The following may have some significance :—

TABLE V.

	ν (calc.).	λ.	ν (obs.).
np'_a—3*s*	12734·5	7848·55 (1)	12737·7
np_a—V	16537·7	6045·09 (2*u*)	16537·8
np_a—$4d_1$	15276·9	6544·51 (1*u*)	15275·7
np_a—$4d_2$	15273·2		
np_b—$4d_1$	14447·2	6920·09 (4*u*)	14446·7
np_c—4*s*	12127·2	8242·27 (1)	12129·3
np_e—J	12128·8		
$2p_1$—np_f	15095·6	6621·61 (4)	15097·9
np_f—R	12485·6	8006·27 (2)	12486·7
$2p_1$—Q	24244·1	4123·27 (2*u*)	24245·8
$2p_2$—E	16063·0	6223·66 (3*u*)	16063·3

The whole arc spectrum from the infra red to λ 3100 has been examined for frequency differences corresponding to the various pairs of terms found in this research. A few were found, but were probably fortuitous. It is, perhaps, important that one of Rydberg's constant frequency differences 680·1 equals the difference between the terms A and B; but there are no terms derivable from this relation which give any further combinations. In all, the difference 680·1 occurs 9 times, 680·0 3 times, 680·2 once. The remainder of Rydberg's doublets are accurately repeated sufficiently often to be considered real, but they have no apparent connexion with the terms calculated in this paper.

Of the lines found experimentally as arc lines in this research, there remain without interpretation:—

λ 2169·49
2171·75
2199·65
2230·071
2238·43
2260·493
2961·177
3093·993

Of these, λ 2169 and λ 2171 seem to form a pair. Considered as due to combinations with md_2, these lines would yield terms 3031·4 and 2983·3. The line λ 1687·2 corresponds sufficiently closely with $1s$—3031·4. If the very strong line λ 2961·177 is due to a transition to md_2, the term 15302·1 may be a companion to E=15709·8, and they might then be an inverted pair of p' terms.

The line given as λ 2199·65 by Hasbach is in reality a double line. A plate, which Professor McLennan has kindly allowed me to use, taken on a Hilger E1 spectrograph, shows, without any doubt, two reversals in this line at λ 2199·57 and λ 2199·73. From the former of these two lines the following combinations may be calculated, using a term V=5656·3:—

	ν (calc.).	λ.		ν (obs.).
md_1—V	45449·2	2199·57	(6R)	45449·2
md_2—V	43406·3	2303·109	(6)	43406·2
$1s$—V	56651·7	1765·5	(3)	56641·2

The wave-number difference between the two components of λ 2199 is 3·2.

The lines usually assigned to combinations with the

f terms in the copper spectrum are very unsatisfactory. In particular the line λ 2369·88, given as $md_2—4f$, does not appear at all in the low-voltage arc though it is a strong line in the arc. It is probably a spark line. The line λ 2260·49, which Dr. Ruark suggested as $md_1— 4f'$, appears faintly in the low voltage arc. The wave-number separation of these two lines is only 2041·0 instead of 2042·9. The lines λ 4056·7 and λ 4015·8, supposed to be $2p_1—4f$ and $2p_2—4f'$, have a separation of 250·9 instead of 248·4, but in this case the error may be due to the broadness of the lines.

The lines λ 3598·01 (2*u*) and λ 3566·14 (1*u*) with a wave-number separation of 248·2 are suggested as $2p_1—5s$ and $2p_2—5s$. In that case $5s=3739·1$.

It is realized that the present investigation of the copper spectrum is not only incomplete but unsatisfactory in that it does not decide the nature of many of the terms found. It is hoped, however, to rectify this by further investigations. The large number of arc lines still unexplained, among them many of great intensity, makes it evident that we are dealing with a spectrum of considerable complexity. It would not be surprising if quartet terms entered into the structure.

Summary.

1. Experiments are described on the ultra-violet spectra of low-voltage arcs in silver and in copper vapour. A table of the lines obtained is given.

2. The line absorption of copper vapour has been found experimentally. Ten lines in the ultra-violet are absorbed. The various combinations calculated from these data are tabulated. No series is evident in these lines.

3. Further terms are calculated from the low-voltage arc lines, using a term $md_1=51105·5$.

Description of Plate.

1. Spectrum of copper arc at 15 volts and 1·2 amperes. This shows some spark lines. The 8-volt plate referred to above has become too scratched for reproduction.

2. Simultaneous photographs of the copper spectrum showing absorption. The arc was at 25 volts and ·5 ampere. On the reproduction, the absorption of the marked lines only is visible.

3. Double reversal in λ 2199·65.

It was impossible to carry out all of the experimental work alone, and I am very grateful to Mr. C. Barnes and others in the laboratory who, on various occasions, kindly assisted me. I am very much indebted to Professor McLennan, who has always given me his interested advice and assistance and who has placed at my disposal all the facilities of the laboratory.

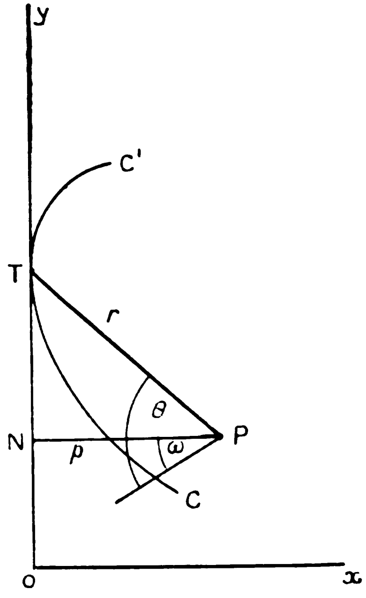
Physics Laboratory,
University of Toronto,
Jan. 13, 1925.

XCVI. *On the Use of Roulettes for Graphical Integration.*

By Alfred A. Robb, *Sc.D.*, *F.R.S.**

Let CC′ be a curve and P a point fixed with respect to it.

Let the tangent at any point T of the curve be taken and let the perpendicular from P to it meet the tangent in the point N.



Let the tangent roll without slipping on the curve, turning in the clockwise direction in the figure.

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* Communicated by the Author.

Let the perpendicular length PN be denoted by p and the angle turned through by p from some fixed direction be denoted by ω.

Let ds be the length of an element of arc of the curve corresponding to an increase $d\omega$ of ω.

Then it is a well-known result that

$$\frac{d^2p}{d\omega^2}+p=\frac{ds}{d\omega},$$

and it is also well known that the length $\mathrm{NT}=\frac{dp}{d\omega}$.

The same formulæ will obviously hold if we suppose the tangent to remain fixed while the curve rolls along it without slipping, but turning in the opposite or anti-clockwise direction in the figure.

Now let us suppose the tangent to be taken as the axis of y of a set of rectangular cartesian coordinates and that the curve rolls along it.

Then, if x and y be taken as the coordinates of P with respect to this set of axes, we have

$$p = x$$

and $$\mathrm{ON} = y.$$

But $$\mathrm{ON} = \mathrm{OT}-\mathrm{NT}$$

$$= \mathrm{OT}-\frac{dp}{d\omega},$$

while $$\mathrm{OT} = s+\text{constant}.$$

Thus $$s-\frac{dp}{d\omega}+\text{constant} = y.$$

Suppose now that the p and ω equations of the curve be expressed in the form

$$\int\frac{f(p)}{p}\,dp+\mathrm{K}=\omega,$$

where $f(p)$ is an arbitrary function of p.

Then

$$f(p)\frac{dp}{d\omega}=p,$$

and so

$$\left(\frac{d^2p}{d\omega^2}+p\right)-\frac{d^2p}{d\omega^2}-f(p)\frac{dp}{d\omega}=0$$

or

$$\frac{ds}{d\omega}-\frac{d^2p}{d\omega^2}-f(p)\frac{dp}{d\omega}=0.$$

Integrating, we get

$$s-\frac{dp}{d\omega}-\int f(p)\,dp = \text{constant}.$$

Thus substituting for p and $s-\frac{dp}{d\omega}$, we get

$$y=\int f(x)\,dx+\text{constant}.$$

If then we can express $\int \frac{f(x)}{x}\,dx$ in terms of known functions, but cannot so express $\int f(x)\,dx$, (a thing which very frequently happens), we can pass from the rolling curve expressed in p and ω coordinates to the relation between y and x for the roulette described by P and so obtain a graphic integration of $\int f(x)\,dx$.

In tracing the rolling curve, the position of the point T is obtained from the relation

$$\mathrm{NT}=\frac{dp}{d\omega},$$

which, when we express $\frac{dp}{d\omega}$ in terms of p, becomes

$$\mathrm{NT}=\frac{p}{f(p)}.$$

If r be the length of the radius vector PT and θ be the angle made by r with the direction (fixed with respect to the rolling curve) from which ω is measured, then

$$\begin{aligned}\tan(\theta-\omega)&=\frac{\mathrm{NT}}{\mathrm{PN}}\\ &=\frac{1}{f(p)}.\end{aligned}$$

But

$$\int\frac{f(p)}{p}\,dp+\mathrm{K}=\omega,$$

and so we get

$$\left.\begin{aligned}\theta&=\int\frac{f(p)}{p}\,dp+\tan^{-1}\left(\frac{1}{f(p)}\right)+\mathrm{K},\\ r&=p\sec\left\{\tan^{-1}\left(\frac{1}{f(p)}\right)\right\}.\end{aligned}\right\}$$

Since the elimination of p between these equations is not generally practicable analytically, it is better to retain p as an auxiliary variable, by means of which we may calculate corresponding values of θ and r and so trace out the rolling curve.

It will be observed that the possibility of doing this depends upon the possibility of expressing $\int \frac{f(p)}{p}\,dp$ in terms of known functions; but we shall show later how we may make use of this result in constructing a general method of graphic integration.

The equation giving r in terms of p may also be written in the (in some respects) simpler form:

$$r = \sqrt{p^2 + \left(\frac{p}{f(p)}\right)^2};$$

but, in addition to the ambiguity of sign introduced by the square root, this is not really so convenient for purposes of calculation, since the former expression may readily be evaluated by means of trigonometrical tables.

As a simple example of the direct application of the above, suppose that we wish to evaluate the logarithmic integral:

$$\int \frac{dx}{\log x},$$

which, as is well known, cannot be expressed by elementary functions.

Put

$$f(p) = \frac{1}{\log p}.$$

Then

$$\int \frac{f(p)}{p}\,dp = \int \frac{dp}{p \log p}$$
$$= \log(\log p) + \mathrm{K}.$$

Thus

$$\left.\begin{aligned} \theta &= \log(\log p) + \tan^{-1}(\log p) + \mathrm{K}, \\ r &= p \sec\{\tan^{-1}(\log p)\}. \end{aligned}\right\}$$

If this curve be traced in polar coordinates and be rolled along the axis of y, then its pole will trace out the curve

$$y = \int \frac{dx}{\log x} + \text{constant}.$$

In practice the rolling curve might be traced on a sufficiently large scale on a stiff piece of cardboard and then cut out carefully.

It might then be caused to roll along a straight edge (preferably faced with rubber to prevent slipping) and fixed so as to coincide with the axis of y on a piece of squared paper. The point of a pencil might then be passed through a small hole in the cardboard at the pole P, and thus the curve

$$y=\int f(x)\,dx$$

might be traced out directly.

If the portion of the rolling curve with which we are dealing is convex to P instead of being concave, as in the figure, then the point P will be situated in a part of the cardboard which will be cut away.

In this case we might fasten the convex-edged piece of cardboard face to face with a second piece of cardboard, so that the two pieces would be at slightly different levels, and a small hole for the pencil point might be made through this second piece at the position corresponding to P. The curve might then be rolled, as in the former case, along the straight edge, and the path of P traced out as before.

Since

$$r=\sqrt{p^2+\left(\frac{p}{f(p)}\right)^2},$$

it will be observed that r becomes infinite for any value of p (or x) which makes $f(x)$ zero; unless x should also at the same time become zero, in such a way that the limit of $\frac{x}{f(x)}$ remains finite. It will therefore be necessary to exclude such points.

It will be observed that this limitation also prevents $\tan^{-1}\left(\frac{1}{f(x)}\right)$ from becoming infinite, since, in order to do so, $\frac{1}{f(x)}$ would require to pass from $-\infty$ to $+\infty$ and back again an infinite number of times; which would entail $f(x)$ becoming zero an infinite number of times.

Again, if for any value of x the integral $\int\frac{f(x)}{x}dx$ becomes infinite, then θ will become infinite and such a point must also be excluded.

We must also suppose that $f(x)$ and $\int \frac{f(x)}{x} dx$ are both continuous within the range of integration, in order that our rolling curve may be continuous.

General Method.

Suppose now that we wish to integrate

$$\int F(x)\, dx,$$

where, for the range under consideration, $F(x)$ is any twice differentiable function of x which is finite, single-valued and continuous; while $F'(x)$ is also continuous.

We shall first take the case where $F'(x)$ is not zero anywhere in the range.

We have

$$\int F(x)\, dx = x\, F(x) - \int x\, F'(x)\, dx.$$

If therefore we write

$$x\, F'(x) = f(x),$$

we have

$$\int \frac{f(x)}{x} dx = F(x) + \text{constant};$$

and so the roulette method of integration may be applied directly to obtain $\int x\, F'(x)\, dx$, which subtracted from $x F(x)$ gives the required integral.

Writing x in place of p and employing inverse cotangents in place of inverse tangents, the equations giving θ and r for the rolling curve then become:

$$\left.\begin{aligned} \theta &= F(x) + \cot^{-1}(xF'(x)) + K, \\ r &= x \sec\{\cot^{-1}(xF'(x))\}. \end{aligned}\right\}$$

When this curve is rolled along the axis of y, its pole will trace out the curve

$$y = \int xF'(x)\, dx.$$

The restrictions placed upon $F(x)$ and $F'(x)$ enable us to construct the rolling curve without θ or r becoming discontinuous or infinite.

The restriction that $F'(x)$ should not be zero is, however, a serious one, which it is desirable to remove.

Now, provided that $F'(x)$ has either a finite lower limit or a finite upper limit for the range, it will always be possible to select some constant C, positive or negative, such that for the range of x under consideration the function

$$F'(x)+2C$$

is always of one sign.

Then we have

$$\int F(x)\,dx = x\,F(x)+Cx^2-\int x(F'(x)+2C)\,dx.$$

Thus if we write

$$x(F'(x)+2C) = f(x),$$

we have

$$\int\frac{f(x)}{x}dx = F(x)+2Cx+\text{constant};$$

and accordingly we may apply the roulette method and obtain

$$\int x(F'(x)+2C)\,dx,$$

which, subtracted from $x\,F(x)+Cx^2$, gives the required integral.

The equations giving θ and r now become:

$$\left.\begin{aligned}\theta &= F(x)+2Cx+\cot^{-1}\{x\,(F'(x)+2C)\}+K,\\ r &= x\sec\left[\cot^{-1}\{x(F'(x)+2C)\}\right].\end{aligned}\right\}$$

The simplest method of tracing this rolling curve is apparently (as in figure) to take a point P and a prime vector through it, from which an angle ω is measured such that

$$\omega = F(x)+2Cx.$$

A length $PN=x$ is then taken along this direction * and a perpendicular drawn to it through N.

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* The projection of PN on the prime vector is obviously

$$x\cos\omega = x\cos\{F(x)+2Cx\}.$$

If we have a table of cosines of angles in radian measure, this enables us to construct the point N very simply on squared paper, without any direct measurement of angles.

Tables of cosines and sines of angles expressed in radian measure have been published by Dr. Carl Burrau (Berlin: Georg Reimer, 1907). In his preface he states (strangely enough) that this is the only table of this kind which has been published.

A point T is then taken on this perpendicular such that

$$NT = \frac{1}{F'(x)+2C};$$

this length being measured off in the direction indicated in the figure, provided that $F'(x)+2C$ is positive.

The aggregate of points such as T is the rolling curve required.

The rolling curve may also be plotted directly in cartesian coordinates: ξ, η, with the point P as origin and the direction from which ω is measured taken as the direction of ξ negative.

If the system be such that the axes of ξ and η may be brought into coincidence with the axes of x and y respectively by motion in their own plane, we have obviously:

$$\left.\begin{aligned}\xi &= \frac{\sin(F(x)+2Cx)}{F'(x)+2C} - x\cos(F(x)+2Cx),\\ \eta &= \frac{\cos(F(x)+2Cx)}{F'(x)+2C} + x\sin(F(x)+2Cx).\end{aligned}\right\}$$

This method of integration possesses the great practical advantage of giving the integral for a whole range of values of the variable in one process, and should thus prove very useful in connexion with many physical investigations where the knowledge of how a function varies over a range is required without extreme accuracy.

On the other hand, the method is probably not very well adapted for use when the analytic form of the function is unknown since, in order to construct the rolling curve in the general case, we require not only the values of $F(x)$ but also of $F'(x)$.

Use of Curvimeter.

The results above obtained may be utilized in a somewhat different manner in effecting the graphical integration of functions.

In the roulette curve

$$y = \int x(F'(x)+2C)dx$$

we may clearly put

$$y = s - \frac{1}{F'(x)+2C},$$

where s is the length (paying due regard to sign) of the portion of the rolling curve involved in the integration. Thus we get:

$$\int F(x)\,dx = xF(x) + Cx^2 + \frac{1}{F'(x)+2Cx} - s + \text{constant.}$$

The length *s* may be measured very accurately with a curvimeter or map-measurer, and the value of the integral may thus be obtained without cutting out the rolling curve.

This method may very likely be preferred to that first described, especially if the form of the rolling curve be complicated.

The most satisfactory form of curvimeter for this purpose appears to be the simple type, consisting of a small serrated wheel turning on a screw axle, which, after tracing out the curve to be measured, is run back to its initial position along a graduated scale, thus giving the length of the line required.

It is to be noted, in using this method, that the length of any portion of the rolling curve in which the curvature is reversed at a turning point is to be regarded as negative.

In case $F'(x)$ is not zero anywhere in the range of integration, we have:

$$\int F(x)\,dx = xF(x) + \frac{1}{F'(x)} - s + \text{constant.}$$

Since in this case $F(x) = \omega$, we see that $xF(x)$ is the length of the circular arc described with radius x and angle ω; and since $\frac{1}{F'(x)}$ is the length of the portion NT of the tangent line to the rolling curve, we may, if we so desire, measure off

$$xF(x) + \frac{1}{F'(x)} - s$$

directly with the curvimeter and so obtain $\int F(x)\,dx$.

XCVII. *Emission Band Spectra of Aromatic Compounds.—Part I. Their Connexion with Infra-Red Absorption Bands and a Classification.* By JOSEPH KENNETH MARSH, *D.Sc.* (*Senior Assistant in Chemistry, the Queen's University of Belfast*) *.

[Plate X.]

THE work in which the writer has been taking a part for the last two years has furnished data with regard to the fluorescence and Tesla-luminescence of a considerable number of the simpler organic substances which are available for examination by these methods (J. Chem. Soc. cxxiii. pp. 642, 817, 2147, 3315 (1923), cxxv. pp. 418, 1743, 2123, (1924); J. Am. Chem. Soc. xlvi. p. 1351; Phil. Mag. xlviii. p. 628 (1924)). The examinations have been conducted upon substances in the vapour state, in which phase greater freedom is obtained for the molecules or their components to vibrate to their natural frequencies, with the consequence that spectra often result showing a much finer structure than those obtained from solutions. Wherever any considerable spectral structure has been observed, it has been found to possess no small degree of regularity, and the object of this paper is to classify the spectra studied, and in the following paper an attempt will be made to give an explanation of their characteristics. Whilst chief emphasis will be laid on emission spectra, when data of the vapour absorption are available use will be made of them, and it will be seen that they lend further evidence to the conclusions arrived at.

The inter-relationship of spectra in the ultra-violet and visible regions with those in the infra-red, forming the basis of Baly's theory of light absorption and fluorescence (Phil. Mag. xxvii. p. 632 (1914), xxix. p. 223 (1915); xxx. p. 510 (1915); xxxi. pp. 417, 512 (1916); xl. p. 1 (1920)), and worked out in some detail by Henri in his book 'Études de Photochemie,' will be further demonstrated. These writers find that the frequency differences between absorption or fluorescence bands are in a number of instances very nearly equal to the absolute frequency of an infra-red band of the same substance, and so regard the former bands as multiples or overtones of the latter. Owing to the fact that emission spectra appear to be very regular, it seems possible to classify them all into a comparatively few types, and to trace the causative agent determining each type. Nevertheless, it must not be thought that these emission spectra lack individual character, for it is very unusual to find two substances of which the spectra cannot be distinguished readily. A good example of each type of spectrum is reproduced in Plate X.

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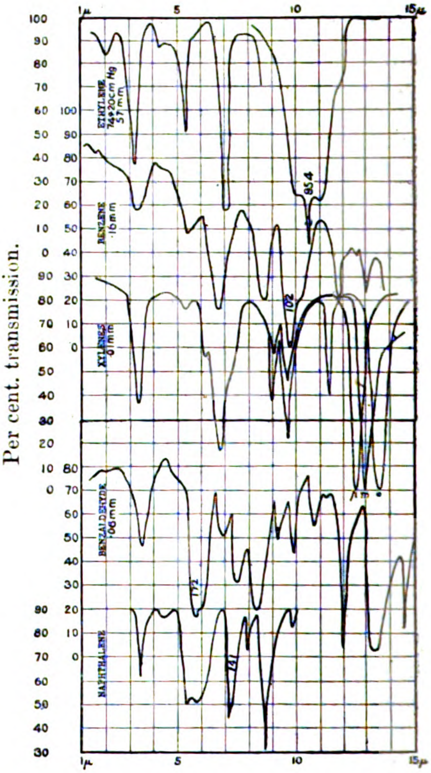
* Communicated by the Author.

TYPE I.—THE BENZENE SPECTRUM. (Pl. X. fig. I.)

Benzene as vapour exhibits series of narrow bands of absorption or fluorescence, the wave-numbers of the former differing from series to series by 92·1 units (Henri, *J. Phys. Rad.* 6, iii. p. 191) and of the latter by 99 units or thereabouts. In addition, the phosphorescence of benzene exhibits bands at regular intervals of the same dimensions, the average being 100 units (Kowalski, *Phys. Zeit.* xii. p. 956 (1912)).

Fig. 1.

Infra-red absorption spectra of typical compounds (after Coblentz and Spence).



Both Baly and Henri consider all these bands to be multiples of the great infra-red band of benzene at 9·8 μ or $1/\lambda$ 102 (Coblentz, 'Investigations of Infra-Red Spectra,' Carnegie Publication No. 35, 1905: see fig. 1 drawn from his curves). For the present we may conclude that the characteristic of the benzene type of spectrum is a succession of bands at intervals of 92 to 100 units; but besides this there is another series at intervals of about 16 units.

TYPE II *a*.—THE ALIPHATIC SUBSTITUENT TYPE. (Fig. II *a*.)

As typical of the spectra of a number of aliphatic substituted derivatives of benzene, that of *p*-xylene may be considered.

p-*Xylene* has, according to Mies (*Zeit. wiss. Phot.* vii. p. 357 (1909)), its chief absorption bands as under. (The figures represent (absolute frequencies) × 3 × 10^{-11}.) The frequency intervals are given in italics.

4186 4146 4109 4066 4028 3987 3948 3908 3869 3830 3792

40 37 43 38 41 39 40 39 39 38 39

80 79 79 78 77

3753 3710 3673 3627 3591

43 37 46 36

80 82

The Tesla-luminescence heads may be arranged thus:

3671 *83* 3588 *38* 3550 *45* 3505 *37* 3468 *45* 3423 *38* 3385

3660 *81* 3579 *38* 3541

3652 *85* *81* 3486

3642 *85* 3557

3605

Kowalski's phosphorescence bands do not appear to show much regularity, but Goldstein's observations of the cathodo-luminescence (*Verh. d. deut. Phys. Ges.* xiv. pp. 33, 493 (1912)) seem to exhibit great uniformity, though his measurements were only made to three significant figures. The following table constructed from his figures shows that the character of the bands is uniform with that of absorption and fluorescence.

2123 2079 2045 2000 1961 1923 1880 1842 1802 1764

44 34 45 39 38 43 38 40 38

78 84 81 78

A difference of about 40 units is found to be the regular interval. Now, this corresponds to the frequency of a band at 25μ which is beyond the limit to which observations have been carried; but a difference of 79, or approximately twice the above, would indicate a band at 12·6μ; and this is just the point at which the strongest band in the *p*-xylene infra-red spectrum is found (see fig. 1). We shall describe other spectra presently to show that *p*-xylene is typical of a group, and also how intimately the ultra-violet bands are related to the infra-red.

TYPE II *b*.—THE TESLA GREEN GLOW. (Pl. X. fig. II *b*.)

A number of aliphatic substituted benzene compounds have been observed to give a characteristic green glow under the Tesla discharge. The spectroscopic examination of this shows that it usually consists of two heads which have a frequency difference of 160 units. The best example of this type is hydrindene where the two bands occur at 1/λ 2119 and 1959. They are also found in indene, in *p*-cymene (one only), in cumene and tetrahydro-naphthalene (but not in naphthalene), and occur in the same positions. It is obvious that they are associated with heavy aliphatic side chains, and the frequency difference supports this conclusion, being just double or quadruple of the differences found for similar substances in the ultra-violet. A corresponding infra-red band is of frequent occurrence at 6·2 μ (1/λ 161·3) in benzene derivatives, though not in aliphatic compounds. The green glow was also observed visually in certain other substances besides those mentioned above, but was not sufficiently strong to photograph. The spectral analysis of the green glow of *p*-xylene differed notably from that of other substances. It contained a number of bands at closer intervals than those mentioned in the instances already given. These still show the ordinary *p*-xylene constant difference of about 40 units. The positions of the bands were 1/λ 2206 2168 2127 2104 2081 2039. The third and last two are probably identical with the three most refrangible bands of the cathodo-luminescence spectrum. Feeble photographic action is detectable down to 1/λ 1850, *i.e.* throughout most of the cathodo-luminescence region.

Having arbitrarily established these types, the grounds for doing so may be indicated by reference to the spectra of a number of other substances. Many of these will be found to possess characteristics showing that the individual spectrum may be a mixture of types.

Toluene.—The Tesla or ordinary vapour fluorescence shows bands which with almost equal validity may be arranged into series of 100 or of 80 unit intervals, as shown in the tables herewith.

3749	3647	3546	3442		3749	3669	3589
3731	3629	3529			3744	3660	
3713	3609			or	3731	3647	3566
3686	3589				3713	3629	3546
3669	3566	3465					
Maximum interval		104.			84		
Minimum	,,	97.			80		
Average	,,	101·5.			82		

These and subsequent arrangements are not made arbitrarily, but with due care to classify the bands as naturally as possible according to their actual appearance on the photographic plates. There are also a few other minor bands which, however, stand alone in either classification and so have been omitted. It will be recognized at once that both the aliphatic derivative and the parent benzene types of spectrum are here present. In the infra-red, Coblentz found bands at 12·03 μ (1/λ 83·1) and 9·73 μ (1/λ 102·8), though neither is particularly strong.

Ethyl Benzene.—Both the vapour fluorescence and absorption are very blurred in character. Again, arrangement of the bands to conform to either type is permissible.

	3669	3569		3689	
3749	3649	3550	3749	3369	3588
3721				3649	3569
3689	3588		3721		3550

Intervals:—

max. 101, min. 100, av. 100·3; max. 82, min. 80, av. 81.

Mesitylene.—The four bands observed in the Tesla-luminescence spectrum can be paired to give intervals of 97 and 99 units. Thus the benzene type is dominant. The benzene bands are also prominent in the infra-red spectrum. (Coblentz, *loc. cit.*)

p-*Cymene.*—The Tesla-luminescence spectrum contains the following bands, which appear to mark the heads of coalesced groups.

3690 *81* 3609 *43* 3566 *43* 3523 *40* 3483

The last three are very indefinite, but it is evident that the recurrent interval is 81 or else about the half of this value, and therefore that the spectrum is of Type II. It will be remembered that the green glow is also found. In the infra-red Coblentz observed a very deep band at 12·25 μ (1/λ 81·7).

Phenol and Anisole.—These two substances gave a number of fluorescence bands, which were arranged according to the benzene type.

		Phenol.			*Anisole.*		
3581	*103*	3478	*95?*	3383?	3639	*99*	3537
3571	*99*	3472			3612	*98*	3514
3553	*103*	3450	*95?*	3355?	3605	*103*	3502
3533	*104*	3429	*108?*	3321?	3576	*102*	3474

Other phenols and phenolic ethers gave almost continuous spectra, so do not lend any help to the present argument.

m-*Xylene.*—Coblentz' study of the infra-red spectra of the three xylenes showed them to have in this region very similar spectra, but the very intense band which occurs at about 13 μ has for each a slightly different position. From what has already been said it appears that the band in this region in the case of *p*-xylene dominates the whole of the spectra observed. If the corresponding band of *m*- and *o*-xylene is also dominant, the spacing of the ultra-violet bands in the three isomers should show variations to correspond with the varying frequency of this infra-red band. The frequencies and intervals of all the bands observed in *m*-xylene are tabulated below.

3741	3697	*75*	3622		3550?
	3687	*71*	3616		
	3678				
	3671	*75*	3696	*75*	3521
	3663				
	3645	*76*	3669		

A good regularity at intervals of about 75 units is shown.

o-*Xylene.*—The fluorescence spectrum is continuous in character, but shows one head and four fairly sharp bands, λλ 3731 3722 3655 3650. These may be paired to show differences of 74 units each.

The following table in connexion with the three xylenes is instructive, and affords striking evidence of the closeness of the relationship of the infra-red bands and the systems found in the ultra-violet.

Substance.	Chief infra-red band.		Av. interval of U. V. bands.
	μ.	ν.	ν.
p-xylene......	12·6	79·4	81
m-xylene......	13·0	76·9	75·2
o-xylene......	13·6	73·5	74

p- *Toluidine* (Pl. X. fig. III.).—Of a number of fluorescence spectra of amines examined, aniline and *p*-toluidine were the only ones which showed any banding. In the *p*-toluidine spectrum there are some eight or nine bands, most of them double, at intervals of about 42 units. Thus the spectrum bears a resemblance to that of *p*-xylene though occurring at greater wave-lengths, and the only structural difference is the attachment of a group weighing 15 in one instance and 16 in the other. In the infra-red the aromatic amines show strong characteristic bands at 6·1–6·15 μ and at 12·2–12·3 μ. Ammonia has a very strong band at 6·1 μ and a deep narrow one at 12·3 μ ($1/\lambda$ 81·3), very similar in position to the characteristic bands of the xylenes, and probably the *p*-toluidine bands may be ascribed to this cause.

Indene resembles toluene and ethyl benzene in having an ultra-violet spectrum of mixed types, though here the aliphatic is perhaps the better developed.

Indene Bands.

3597	*76*	3521	*79*	3442	*72*	3370		3597	*102*	3495	*103*	3392
3590	*75*	3515	*77*	3438				3590	*101*		*100*	3389
3584	*75*	3509					or	3584				
3570	*75*	3495						3570	*100*	3470	*100*	3370
		3470	*78*	3392						etc.		
		3463	*74*	3389								

Hydrindene has, besides the green glow already mentioned, other bands in the ultra-violet of the type found in aliphatic substituted benzene derivatives.

Hydrindene Bands.

3701			
3690	*76*	3614	*47*
		3607	
3675	*77*	3598	
		3585	

Phenyl Acetylene.—The Tesla-luminescence bands show a resemblance to benzene.

3588	*51*	3535	*102*	3435			
3570	*45*	3525	*99*	3426	*104*	3322	
3540	*52*	3488					3190

Styrene.—The Tesla spectrum is distinctly of the benzene type, though not a large number of bands are seen.

3490	3482	3475	3459	3453	3413	3407
		98	*102*	*98*	*102*	
		3377	3365	3355	3311	

This might be expected, for neither this substance nor the last has a true aliphatic group, and the band at about 10 μ in benzene is also very strong in ethylene; in fact, it seems not improbable that this infra-red band is a characteristic of a carbon atom with only three valencies satisfied rather than of a benzene nucleus. This subject will be discussed further in the following paper.

The *Methyl Naphthalenes* gave a Tesla spectrum in the red region which appears to be the naphthalene counterpart to the green glow of aliphatic derivatives of benzene. Just as the previously known spectra of naphthalene occur at greater wave-lengths than in benzene, so also does this newly-observed glow. The highest frequency head of naphthalene vapour fluorescence is at 1/λ 3245, and the first head of the green glow at 1705, whereas the benzene fluorescence spectrum begins at 3749, and the green glow of derivatives at 2119. The interval in the former case amounts to 1500 and in the latter to 1630. No corresponding glow has been observed in anthracene derivatives. The first strong ultra-violet fluorescence head is at 2758, and it will be found on calculation that an interval of similar dimensions to that obtaining between the ultra-violet and visible heads in benzene or naphthalene and their derivatives would indicate a wave-length for the glow of anthracene lying in the infra-red.

TYPE III.—THE BLUE BANDS. (Pl. X. fig. V.)

A considerable number of substances examined for Tesla-luminescence have given a blue spectrum which consists of a number of bands, but is chiefly characterized by three of great strength at regular intervals of 173 units of frequency. This spectrum is not excitable to more than a slight extent, if at all, by light.

Benzaldehyde is the outstanding example of the type, and may be considered first. The absorption spectrum consists of three bands at 1/λ 4098 3565 3049 respectively (Steiner, *Comp. Rend.* clxvi. p. 744 (1913)) showing intervals of 516 and 533. The first blue band is at 2519, an interval from the nearest absorption band of 530, without making allowance for passing from measurements in solution to those in vapour. The other blue bands of the series are at 1/λ 2346 2175 2004, the four having average intervals of 172·3, and in the infra-red there is a strong band at 5·84 (1/λ 171·2). It will be seen that the intervals between the absorption bands are approximately three times those between the blue bands.

Except in the case of acetophenone and anisaldehyde, where in place of the usual comparatively sharp bands a much more diffuse spectrum is found, the blue bands of all the substances examined are very similar in position and appearance apart from intensity. Moreover, they lie in a region by themselves, and so are not found superposed on other types, though they may be accompanied by them.

An interesting variation was found in the case of benzoquinone. This substance gave a yellow glow under the Tesla discharge, and the following bands were observed :—

1872 1699 1623 1564 1534

The first two and the last were strong, and show intervals of 173 and 165 units. Considering the small accuracy with which measurements could be made with the quartz spectroscope in this region, agreement with the usual interval of about 173 units would seem to be maintained.

TYPE IV.—THE CONDENSED NUCLEI. (Pl. X. fig. IV.)

As an example we shall take *Anthracene*, the Tesla-luminescence of which is in the most sensitive photographic region and is of exceptional intensity, a few seconds sufficing to photograph it. Several bands are seen; they occur at $1/\lambda$ 2882 2758 2618 2465 2326. The intervals between the last four are respectively 140 143 139 units. The absorption spectrum has bands at 2654 2796 2938 3076, the respective intervals being 142 142 138. The same interval as in emission is here evident. The infra-red spectrum has not been studied with success, and the most nearly related substance of which the spectrum has been mapped in this region is naphthalene.

Naphthalene.—The fluorescence bands recorded by Dickson (*Zeit. wiss. Phot.* viii, p. 247 (1910)), fourteen in number, show a perfectly regular spacing at intervals of 47 units. A cursory examination of naphthalene fluorescence in chloroform solution made by Mr. W. H. McVicker showed seven or eight of these bands, and moreover gave grounds for stating that every third one was stronger than its neighbours—*i. e.*, there is also a regularity at intervals of 141 units, as in anthracene. The vapour-emission spectra of naphthalene do not show narrow banding. This is the only instance yet found where the vapour gives rise to a less detailed spectrum than the solution. In a recent study of naphthalene vapour absorption, Henri and Làszlò (Proc. Roy. Soc. A, cv. p. 662 (1924)), find the same interval of 47·4 units between many of the chief bands as is found in solution fluorescence.

The infra-red spectrum of naphthalene has been examined by Stang (Phys. Rev. ix. p. 542 (1917)), and shows a strong band at 7·19 μ (1/λ 139·1). Many of the benzene bands are also found, but the band at 7·19 is among the strongest, and persists in most of the simple derivatives which he examined. There can be little doubt that this band is characteristic of naphthalene, and probably of anthracene and other nuclei also. Numerous anthracene derivatives have recently been examined, and their Tesla-luminescence spectrum usually shows as the main feature the anthracene bands, but often with slight variations in position. Octahydroanthracene and tetrahydronaphthalene are interesting derivatives which have been studied. In both cases the spectral character has reverted to Type II., the aliphatic substituted benzene type.

Besides the substances which it has been possible to place in one of the classes enumerated in the preceding pages, there are very many which give only continuous spectra. Certain groups prevent emission spectra from developing at all, and of the rest some more than others tend towards the production of continuous spectra, but with increasing complexity a stage of complete continuity is always soon reached. Probably in no substance examined are there less than two superimposed types of oscillation. Further study will reveal the theoretical significance of the present classification, but this is deferred to the following paper.

Abstract.

The paper is largely a commentary on previous work by the author and collaborators. The spectra studied are shown to be capable of classification into :—(1) A benzene type, characterized by bands at frequency intervals of 102 and 15·9 waves/mm. (2) A benzene aliphatic-derivative type with band intervals of 40 or 80 in the ultra-violet. These substances under the Tesla discharge also usually give a green glow consisting of two bands at an interval of 160. (3) "The Blue Bands"—a spectrum produced by the Tesla discharge through a number of substances of which benzaldehyde is an outstanding example, characterized by three very strong bands at intervals of 172 units. (4) A condensed nuclei type, perhaps not so well established. Anthracene and derivatives show three or four characteristic bands near 4000 Å.U. at intervals of 142 units, whilst naphthalene has a series of bands at one-third of this interval. Many substances do not give any emission, or only one of a continuous character, and so cannot be classified. It is shown that in the infra-red, bands of absolute frequency equal to the above ultra-violet frequency differences are in each case well marked and characteristic.

XCVIII. *Quantum Magnetic Tubes in Rotation. By* H. STANLEY ALLEN, *M.A.*, *D.Sc.*, *Professor of Natural Philosophy in the University of St. Andrews* *.

QUANTUM Theory requires an atomicity in nature of a kind not previously suspected †. It is probable that this atomicity is intimately related to the existence of positive and negative electrons, a fact which is not as yet satisfactorily explained. It has been shown in earlier papers ‡ that the theory of quanta suggests the existence in three dimensions of discrete tubes of magnetic induction, corresponding to the "magnetic lines" which Faraday conceived of as physical entities, or in four dimensions of discrete electromagnetic tubes of force, the "calamoids" of Prof. E. T. Whittaker §. It is the object of the present communication to discuss the properties of quantum magnetic tubes rotating about an axis, to determine their angular momentum and energy, and to consider the electrostatic field set up by their rotation and the possible connexion between such a rotating tube and an electron. It may be said at the outset that the paper is frankly speculative in character.

§ 1. MAGNETIC TUBES IN ROTATION.

Towards the end of 1920 Professor E. T. Whittaker drew my attention in conversation to the nature of the electrostatic field which would be set up by magnetic tubes in rotation. He pointed out that if a set of magnetic tubes, such as would be produced by a small current circuit, or a small magnet, could be supposed to rotate like rigid wires about the axis of symmetry, an electric field would be produced which in the equatorial plane would vary inversely as the square of the distance from the centre of the system.

A large number of such systems oriented at random would produce, on the average, an electric field at a distance similar to that due to an electrostatic charge, that is, a field varying inversely as the square of the distance. The "equivalent" electrostatic charge for a single system would be proportional to the magnetic moment (M) of the elementary magnet, and the angular velocity (ω) with which the system is rotating.

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* Communicated by the Author.

† J. H. Jeans, 'Report on Radiation and the Quantum Theory,' Chapter 8.

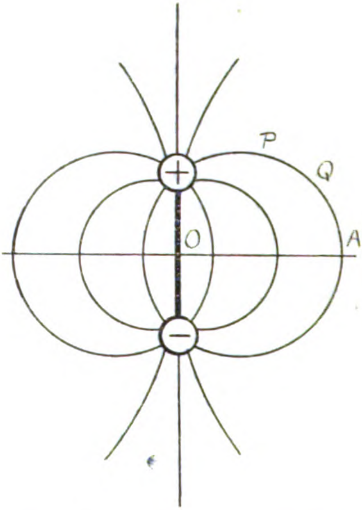
‡ H. S. Allen, Phil. Mag. xlii. p. 523 (1921), xlviii. p. 429 (1924); Proc. Roy. Soc. Edin. xlii. p. 213 (1922).

§ E. T. Whittaker, Proc. Roy. Soc. Edin. xlii. p. 1 (1921).

Further, Whittaker drew attention to the remarkable fact that for a given direction of the axis of the magnet there were *two* possible directions of rotation for the magnetic tubes, thus suggesting the possibility of interpreting the difference between positive and negative electric charges.

An obvious difficulty in the way of applying this conception to the classical magnetic tubes associated with an elementary magnet lies in the fact that at a great distance from the magnet the tubes would be moving with a velocity exceeding the velocity of light. This difficulty, however, does not arise if we adopt the view now advocated of the existence of discrete quantum tubes, for we need consider the rotation of only a limited number of such tubes, or even that of a single quantum tube. Thus we may in imagination isolate a single quantum tube, such as the one indicated in fig. 1 passing through the points P and Q, and discuss the electric field associated with that particular tube, the velocity of P being less than that of light, even in the limiting case in which the velocity of the point A in the equatorial plane approaches the velocity of light.

Fig. 1.



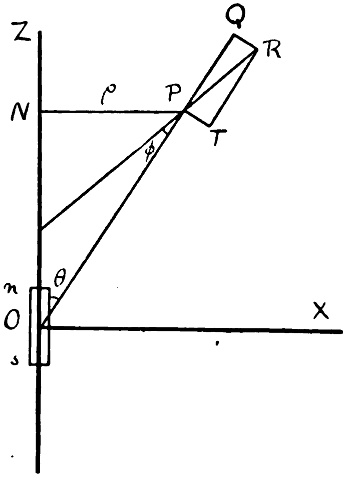
At this point an interesting comparison is suggested between the rotation of such quantum tubes and the rotation of an electron in one of the circular orbits in Bohr's theory.

We know that in that theory an orbit with a large value for the quantum number corresponds to a velocity less than the velocity of light. Also an important question is suggested as to the greatest distance at which electrostatic effects have actually been observed. In the classical theory it is always assumed that the field of an electric charge extends to infinity, but it would be interesting to know what experimental evidence there is bearing on this point.

§ 2. A QUANTUM MAGNETIC TUBE IN ROTATION.

We consider a single quantum tube such as would originate in a small magnet of magnetic moment M, and suppose it to be rotating with angular velocity ω about the axis of the magnet. Let A be the area of cross-section,

Fig. 2.



ds the length of an element of the tube at any point P, determined by the coordinates r, θ.

The mass associated with each unit of volume of a magnetic field* is $KB^2/4\pi$, consequently the mass of an element of the tube at P is $\frac{KB^2}{4\pi}A\,ds$. Draw a perpendicular PN from P to the axis of the magnet, and let the length of this perpendicular be ρ. Then the angular momentum of the element about the axis is $\frac{\mathrm{KB}^2}{4\pi}\mathrm{A}ds \times \rho^2\omega$. Now for a quantum tube the flux of magnetic induction, $\mathrm{BA}=\mu\mathrm{HA}=h/e$, and is constant along the tube. Therefore the angular momentum reduces to

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* In this paper the electric and magnetic coefficients K and μ will be retained in the analysis.

$$\frac{\mathrm{K}\mu}{4\pi}\cdot\frac{h}{e}\cdot\omega\cdot\mathrm{H}\rho^2 ds.$$

The angular momentum for the whole tube is found by integrating this expression throughout the length of the tube.

Evaluation of the Integral $\int \mathrm{H}\rho^2 ds$.

The strength, H, of the magnetic field at P may be found by resolving the magnetic moment, M, along and perpendicular to OP. Thus we find that the field at P is made up of two components in these two directions. The former component, that is the component represented by PQ in the diagram, is given by $\frac{2\mathrm{M}\cos\theta}{\mu r^3}$; the latter component is $\frac{\mathrm{M}\sin\theta}{\mu r^3}$, represented in the figure by the line PT perpendicular to OP, so that the resultant magnetic field, H, is represented by PR.

Thus
$$\mathrm{H}=\mathrm{PR}=\sqrt{(\mathrm{PQ}^2+\mathrm{PT}^2)}$$
$$=\frac{\mathrm{MR}}{\mu r^3}\sqrt{(1+3\cos^2\theta)}.$$

The inclination of this resultant force to the line OP is $\mathrm{R}\hat{\mathrm{P}}\mathrm{Q}=\phi$, where

$$\tan\phi=\frac{\mathrm{RQ}}{\mathrm{QP}}=\frac{\mathrm{PT}}{\mathrm{PQ}}=\frac{\sin\theta}{2\cos\theta}=\tfrac{1}{2}\tan\theta.$$

It is easily shown that

$$\sin\phi=\frac{\sin\theta}{\sqrt{(1+3\cos^2\theta)}}.$$

Now turning to the integral $\int \mathrm{H}\rho^2 ds$ we have

$$\rho=r\sin\theta \text{ and } ds=rd\theta/\sin\phi,$$

and substituting in the integral we get

$$\int \mathrm{H}\rho^2 ds = \int \frac{\mathrm{M}}{\mu r^3} \sqrt{(1+3\cos^2\theta)}\, r^2 \sin^2\theta\, ds$$

$$= \frac{\mathrm{M}}{\mu} \int_0^\pi \frac{\sqrt{(1+3\cos^2\theta)}\sin^2\theta\, d\theta}{\sin\phi}$$

$$= \frac{\mathrm{M}}{\mu} \int_0^\pi (1+3\cos^2\theta)\sin\theta\, d\theta$$

$$= -\frac{\mathrm{M}}{\mu}\Big[\cos\theta + \cos^3\theta\Big]_0^\pi$$

$$= \frac{4\mathrm{M}}{\mu}.$$

Substituting this value in our expression for the angular momentum, we find that the total angular momentum for the single quantum tube is

$$\frac{\mathrm{K}\mu}{4\pi} \cdot \frac{h}{e} \cdot \omega \cdot \frac{4\mathrm{M}}{\mu} = \frac{\mathrm{KM}}{\pi} \cdot \frac{h}{e} \cdot \omega.$$

We notice that the magnetic tube which we are considering has an equivalent moment of inertia

$$\mathrm{I} = \frac{\mathrm{KM}h}{\pi e}.$$

Remembering that the angular velocity, ω, can be expressed in terms of the frequency by writing $\omega = 2\pi\nu$,

$$\text{the Angular Momentum} = \frac{2\mathrm{KM}h}{e}\nu.$$

The kinetic energy of the quantum tube is obtained by multiplying the angular momentum by $\frac{1}{2}\omega$, and so we find

$$\text{the Kinetic Energy} = \frac{1}{2}\frac{\mathrm{KM}h}{\pi e}\omega^2 \text{ or } \tfrac{1}{2}\mathrm{I}\omega^2,$$

$$= \frac{2\pi\mathrm{KM}h}{e}\nu^2.$$

§ 3. ELECTROSTATIC FIELD OF A ROTATING TUBE.

When a magnetic tube is in motion, it produces an electric field. In the case of the rotating quantum tube already considered the electric field set up at a point A in the equatorial plane is equal to Bv, where v is the velocity of the rotating tube at that point. If the distance OA is a, the velocity $v=a\omega=2\pi a\nu$, and thus the electric field is $\mathrm{B}a\omega$, or $2\pi a\mathrm{B}\nu$.

Let us assume that the electric field at A is the same as would be produced by an electrostatic charge E at the point O, and then determine the value of that charge. Since the two fields are assumed to be equal,

$$\frac{\mathrm{E}}{\mathrm{K}a^2}=\mathrm{B}v=\mathrm{B}a\omega=2\pi a\mathrm{B}\nu.$$

Now the magnetic field at A is supposed to be due to an elementary magnet of moment M, so that the strength of the magnetic field is $\mathrm{M}/\mu a^3$. Thus at the point A,

$$\mathrm{B}=\mu\mathrm{H}=\mathrm{M}/a^3.$$

Hence

$$\frac{\mathrm{E}}{\mathrm{K}a^2}=\frac{\mathrm{M}}{a^3}v,$$

or, since $v=a\omega$,

$$\frac{\mathrm{E}}{\mathrm{K}a^2}=\frac{\mathrm{M}}{a^2}\omega.$$

Therefore we have

$$\frac{\mathrm{E}}{\mathrm{K}}=\mathrm{M}\omega.$$

Thus the *equivalent charge* at O is given by $\mathrm{E}=\mathrm{KM}\omega$.

This relation may now be used in expressing the angular momentum of the rotating quantum tube.

$$\text{Angular Momentum}=\frac{\mathrm{KM}}{\pi}\cdot\frac{h}{e}\cdot\omega$$

$$=\frac{\mathrm{E}}{e}\cdot\frac{h}{\pi}.$$

If we assume that the charge $\mathrm{E}=\mathrm{Z}e$, expressing the charge in terms of the electron charge e, then the Angular Momentum $=\mathrm{Z}\times h/\pi$.

The Kinetic Energy of the tube takes the simple form

$$\frac{1}{2}\frac{\mathrm{E}}{e}\cdot\frac{h}{\pi}\cdot\omega$$

$$=\frac{\mathrm{E}}{e}\cdot h\nu,\quad\text{since }\omega=2\pi\nu,$$

$$=\mathrm{Z}h\nu.$$

If, in the above results, we take $\mathrm{Z}=1$, so that the equivalent charge equals the electron charge e, we find for the angular momentum of the rotating tube h/π, and for the kinetic energy $h\nu$. It is important to observe that these values are exactly double those obtained by adopting Nicholson's quantum condition which postulates a natural unit of angular momentum of magnitude $h/2\pi$, corresponding to an amount of kinetic energy $\frac{1}{2}h\nu$. We have, in the present case, an amount of energy corresponding to Planck's quantum $h\nu$. We may compare the results we have obtained with those in the case of the simple Bohr atom, where the *kinetic* energy of the circulating electron is $\frac{1}{2}h\nu$ and the *potential* energy is numerically double this amount. It may be pointed out that in our present work we are virtually expressing potential energy in terms of what, from the ordinary standpoint, would be described as concealed kinetic energy.

§ 4. ELECTRONS REGARDED AS ROTATING TUBES.

It is instructive to take some numerical examples of these results.

Case I.—According to the principle of relativity the energy corresponding to a mass m as judged by an observer relatively at rest is mc^2. Let us assume that in the case of a negative electron this amount of energy may be identified with the energy of rotation of a single magnetic tube. This corresponds to the assumption made by Stark [*], who identified the equivalent energy of an electron at rest with one quantum of energy $h\nu$. Then we have

$$h\nu = mc^2.$$

Taking

$$h = 6{\cdot}558 \times 10^{-27} \text{ erg sec.},$$

$$m = 9 \times 10^{-28} \text{ gm.},$$

$$c = 3 \times 10^{10} \text{ cm./sec.},$$

this yields for ν, the frequency of rotation, the value $1{\cdot}24 \times 10^{20}$ sec^{-1}. That is, a single quantum tube rotating with this frequency would have an amount of inertia equal to that of a negative electron.

The frequency in question may be expressed in a different way by using the fundamental Rydberg frequency

$$\nu_0 = \frac{2\pi^2 me^4}{h^3 K^2}.$$

Putting

$$\frac{2\pi e^2}{hcK} = \alpha,$$

where α is a pure number, we may write

$$mc^2 = \frac{2h\nu_0}{\alpha^2}.$$

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[*] Stark, *Phys. Zeitschr.* viii. pp. 881-884 (1907).

The form of this result suggests that the amount of the energy mc^2 associated with the mass of the electron may be regarded as a quantum of energy $h\nu$, provided $\nu=\frac{2\nu_0}{\alpha^2}$.

If we further assume that the maximum velocity of the rotating tube approaches the velocity of light, we can form an estimate of the size of our electron. This means that the velocity of the point A is supposed to approach the velocity of light, so that $v=a\omega=c$. Consequently, ω being $2\pi\nu$, $2\pi\nu a=c$, and thus

$$a=\frac{c}{2\pi\nu}=\frac{c}{\frac{4\pi\nu_0}{\alpha^2}}=\frac{\alpha^2 c}{4\pi\nu_0}=3\cdot 86\times 10^{-11}\text{ cm.}$$

A more convenient expression for the radius is obtained in terms of the innermost orbit in Bohr's theory of the hydrogen atom. This may be written

$$a_1=\frac{\alpha c}{4\pi\nu_0}.$$

Therefore $\qquad a=\alpha a_1$.

Assuming $e=4\cdot 774\times 10^{-10}$ E.S.U. the numerical value for α is 1/137. The radius of the electron is 1/137 times the radius of this innermost orbit.

From the relation $E=KM\omega$ the magnetic moment of the elementary magnet is found to be

$$M=\frac{\mu he}{2\pi m}.$$

This is twice the magnetic moment of the Bohr magneton, and it may be mentioned that it corresponds very closely with the value derived from the saturation intensity of magnetization of iron, which according to Ewing[*] is nearly 2×10^{-20} c.g.s. units per atom of iron.

The ratio of the angular momentum to the magnetic moment for the electron here considered has the value $2m/\mu e$, which is equal to the gyromagnetic ratio deduced from the theory of electron orbits by O. W. Richardson[†].

Case II.—In the preceding calculations we have neglected the energy associated with the frequency characteristic of the tube itself, energy which may correspond, possibly, to an internal vorticity. When this is taken into account we have to deal with an amount of energy $h\nu_r$ due to the rotation of the whole tube about an axis with frequency ν_r, and also an amount of energy $\frac{1}{2}h\nu_s$ which is due to the internal condition of the tube, and would be present in the tube when not rotating, ν_s being the frequency appropriate to the stationary tube[*]. These quantities are additive, and as there are two possible directions of rotation we have for the energy in one case $h\nu_r+\frac{1}{2}h\nu_s$, and in the other $h\nu_r-\frac{1}{2}h\nu_s$. As the first amount is clearly greater than the second, let us identify the first case with a positive electron, the second with a negative electron.

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[*] J. A. Ewing, Proc. Roy. Soc. Edin. xlii. p. 124 (1922).

[†] O. W. Richardson, Phys. Rev. xxvi. p. 248 (1908); Proc. Roy. Soc. cii. p. 538 (1923).

Let m_P be the mass of the proton (+ve electron), and m_C the mass of the corpuscle (−ve electron). Then, in accordance with the principle of relativity,

$$m_\text{P}c^2=h\nu_r+\tfrac{1}{2}h\nu_s$$

$$m_\text{C}c^2=h\nu_r-\tfrac{1}{2}h\nu_s.$$

That is to say, we have here expressions for the mass of the proton and the corpuscle expressed in terms of these two frequencies ν_r and ν_s. Dividing the first by the second we get at once

$$\frac{m_\text{P}}{m_\text{C}}=\frac{2\nu_r+\nu_s}{2\nu_r-\nu_s},$$

and therefore
$$\frac{m_\text{P}+m_\text{C}}{m_\text{P}-m_\text{C}}=\frac{2\nu_r}{\nu_s}.$$

The value found experimentally for $\frac{m_\text{P}}{m_\text{C}}$ is very nearly 1833 (Bucherer and Ladenburg). Using this numerical value we find $\frac{\nu_r}{\nu_s}=0{\cdot}50051$. This means that the frequency of rotation of our magnetic tube is rather larger than one-half the frequency characteristic of the stationary tube.

It is convenient, as in Case I., to express the frequency in terms of the fundamental Rydberg frequency

$$\nu_0=\frac{2\pi^2me^4}{h^3K^2}$$

by means of the relation

$$mc^2=\frac{2h\nu_0}{\alpha^2}.$$

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[*] H. S. Allen, Phil. Mag. xlii. p. 523 (1921)

From the equations we find without difficulty the results

$$\left.\begin{aligned}\nu_r &= \frac{\nu_0}{\alpha^2}\left(\frac{m_P}{m_C}+1\right)\\ \nu_s &= \frac{2\nu_0}{\alpha^2}\left(\frac{m_P}{m_C}-1\right)\end{aligned}\right\}.$$

Substituting the numerical values

$$\nu_0 = 3\cdot271\times10^{15},\quad 1/\alpha = 137,$$

we find

$$\left.\begin{aligned}\nu_r &= 1\cdot126\times10^{23}\ \text{sec.}^{-1}\\ \nu_s &= 2\cdot250\times10^{23}\ \text{sec.}^{-1}\end{aligned}\right\}.$$

If we assume, as in Case I., that $a\omega_r = c$, we find as a limiting value for a, the radius of the electron, $4\cdot24\times10^{-14}$ cm. It should be noticed that on these assumptions the size of a negative electron does not differ from the size of a positive electron, the radius being a quantity of the same order of magnitude as was obtained by Rutherford, from experiments on the scattering of α particles, to represent the size of an atomic nucleus. The radius of the negative electron on the classical theory is well-known to be a quantity larger than this, but that estimate is derived from the assumption that the electron may be treated as a charged sphere.

Although no quantitative explanation has yet been found for the frequencies ν_r and ν_s, which have been assigned so as to give the masses actually observed, it may be suggested that they are in some way determined by the limiting condition that the velocity of the extreme edge of the rotating tube cannot exceed the velocity of light.

It is interesting to compare with the suggestions here made a surmise as to the relation between positive and negative electricity put forward independently by Sir Oliver Lodge * in his Presidential Address to the Röntgen Society on 6th November, 1923.

"Let us suppose then that round the nucleus of an atom the ether is in a state of violent rotation. It might even be suggested that a proton itself is always and constitutionally in a state of circulation at a speed comparable to the velocity of light, and that in this way its mass is accounted for, as distinguished from the much smaller mass of the electron, which presumably is not in a state of rotation. We might go so far as to surmise—as indeed we do for many other reasons, connected with the transmission of waves by a vortex filled medium—that the normal ether contains a constitutional rotation comparable to the velocity of light, and

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* Brit. Journ. of Radiology, vol. xx., Jan. 1924.

that upon this, when a pair of electric units are being somehow generated, two equal opposite rotations are superposed; one in opposition to the original rotation, giving a result slightly nearer to the velocity of light than before, conceivably sufficient to cause what would otherwise be the mirror-image of the negative electron to have a mass 1,850 times as big."

§ 5. Discussion of suggested Electronic and Atomic Models.

In considering the model here put forward, attention may be drawn to a paper by H. Bateman [*]. He remarks that an electron rotating on its axis like a planet does not radiate as much as when not rotating. "The fact that the radiation is reduced by rotation may indicate that revolving electrons do rotate."

It will have been noticed that the fundamental electric charge here postulated possesses axial and not spherical symmetry. Further, it must possess magnetic as well as electric properties. In this connexion reference may be made to a paper by Duane [†], in which a calculation is made of the velocity of projection of α particles on the assumption that atomic nuclei may be regarded as small magnets, the resulting velocity being of the order of magnitude observed experimentally. Reference may also be made here to the important work of Stern and Gerlach, who have deduced from their experiments the magnetic moment of the normal silver atom in the gaseous state as being one Bohr magneton. This magnetic moment is usually supposed to be due to what may be called the outer, or loosely bound electrons.

The picture of *an atomic nucleus* suggested by the foregoing considerations is that of a set of magnetic tubes rotating about a common axis with the same angular velocity, some of the tubes representing positive, the remainder—the smaller number—negative electrons.

Outside the nucleus we should expect to have in addition a set, or sets, of outer magnetic tubes, of larger size, rotating or capable of rotating about the same axis so as to give rise to the external magnetic and electric field due to the atom. These tubes may be supposed to rotate with very much smaller angular velocity than the inner set. For instance, they might have an angular velocity comparable with that of the radius vector to an electron in one of the Bohr orbits. In that case the mass to be associated with these outer tubes would be very small in comparison with the mass of the nucleus.

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[*] Nat. Acad. Sci. Proc. v. p. 367 (1919).

[†] Duane, Phys. Rev. v. p. 335 (1915).

According to the hypothesis advanced *each quantum tube may be regarded as a potential electron.* In a former paper[*] it was suggested that the emission of radiation consisted in, or was consequent upon, the liberation of a quantum tube from an atomic or molecular system. Taking this suggestion in connexion with the present hypothesis, some light is thrown on the remarkable reciprocal relation between radiation and electrons. With characteristic boldness Sir Oliver Lodge[†] discussed this problem in an address on Ether and Electrons, and suggested that the actual generation of an electron by means of light is not an altogether impossible idea.

Further, the results and suggestions of the present paper may be considered in relation to the "Quantum Mechanism in the Atom" described by Prof. Whittaker. For the magnetic wheel in rotation, used as an illustrative model, is equivalent to a set of rotating magnetic tubes, and the structure is essentially a mechanism by which an electrostatic field is produced by the motion of these tubes. Stress may be laid on Prof. Whittaker's argument that when an electron is approaching an atom, the electric field about the atom is not permanent, but is evoked by the approach of the electron. The electron induces within the atom a "magnetic current," *i. e.* the magnetic analogue of an electric current.

Also it is worthy of special note that in this mechanism the electric separation in the atom, which is caused by the collision with the bombarding electron, is precisely a separation of two electronic charges $+e$ and $-e$. The process might be described as the manufacture of a positive and negative electron, or at least as a stage in such manufacture. Again, the emission of radiation by the mechanism may be regarded as the liberation of a magnetic tube from the structure.

"Until fuller certainty comes, it is well that every hypothetically possible line of advance should be explored"[‡]. The suggestions of this paper are put forward in the conviction that these words are in a special sense true at the present stage in the development of physical theory.

The University,
St. Andrews,
6 March, 1925.

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[*] H. S. Allen, Phil. Mag. xlviii. p. 429 (1924).

[†] Sir Oliver Lodge, 'Nature,' cxii. p. 185, August 4th, 1923.

[‡] W. Peddie, Proc. Roy. Soc. Edin. xlii. p. 223 (1922).

XCIX. *A Space Charge Effect.* *By* E. W. B. Gill, *M.A., B.Sc., Fellow of Merton College, Oxford* *.

1. If in a 3-electrode gas-free valve the grid and plate are both maintained at a positive potential with regard to the filament, the grid potential being the higher, then when the filament is heated, the electrons which leave it move towards the grid, some are collected on the grid, and the remainder pass through it and are collected on the plate.

If the plate potential is only a few volts, and if n_1 is the number of electrons reaching the grid per second, n_2 the number reaching the plate, it is found in general that the ratio $\frac{n_1}{n_1+n_2}$ is constant if n_1+n_2 is varied, this last being the total number leaving the filament, which is controlled by the filament temperature. That is, a fixed proportion of the current from the filament reaches the plate.

Thus with a Mullard Valve in which the grid was kept at 40 volts and the plate at 6 volts (the negative end of the filament being taken as zero potential), the following results were obtained, the currents being measured in milliamperes:

Total emission from filament	2·5	5	7·5	10	15	20
Current received by plate...	1·3	2·6	4·0	5·3	7·9	10·6

while with the plate at 10 volts and the grid still at 40, the results were:

Total emission	2·5	5	7·5	10	15	20
Plate current	1·4	2·7	4·1	5·5	8·2	10·9

In the first case the plate received 53 per cent. of the total emission, the grid receiving the other 47 per cent., these proportions being independent of the emission. In the second case the plate received a slightly higher proportion, 54·5 per cent. of the total.

The total current n_1+n_2 passing across the valve cannot be increased beyond a certain limit, which is reached when the space charges and the fixed potentials together make the electric force zero at the filament, as in Langmuir's well-known calculations.

2. The Mullard valve used had a cylindrical grid of diameter about 4 mm., the plate being a cylinder of 1 cm. diameter. If the above experiment be tried with a valve in which the plate is a good deal larger in diameter than the

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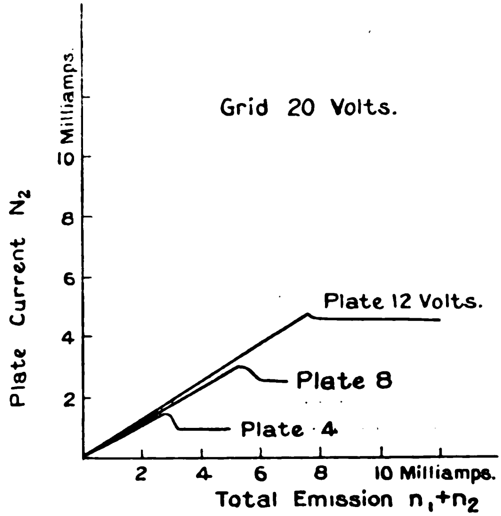
* Communicated by Professor Townsend.

grid, the results are entirely different. The valve used in the experiments to be described was made by the Marconi Company, and had a grid of 5 mm. diameter, and a plate of 2·5 cm. diameter. Thus the ratio of plate diameter to grid diameter, which in the Mullard valve was 2·5, was 5 in the Marconi valve.

The filament was electrically heated to various temperatures by varying the potential across it from about 4 to 6 volts. The results obtained are shown in figs. 1, 2, 3. The three curves in fig. 1 represent the results of experiments with the grid at 20 volts and the plate at 4, 8, and 12 volts, the ordinates being the current n_2 to the plate and the abscissæ the total current n_1+n_2. The curves in fig. 2 represent the results of experiments which were done exactly under the same conditions, except that the grid was at 30 volts, while in fig. 3 the grid was at 40 volts. (It should be noted that the plate potentials are so low that the effect of secondary emission from the plate is negligible.)

Fig. 1.



If the results for the Mullard valve were plotted in the same way the curves would be straight lines through the origin n_2 being always proportional to n_1+n_2, but with the Marconi valve only the first portions of the curves are straight lines. With the grid at 20 volts and the plate at 4 volts, the plate current n_2 is only proportional to the total emission n_1+n_2 when it is less than 1·6 milliamps. With the plate at 8 volts the proportionality holds till the plate current is 3 milliamps., while 5 milliamps. is the limit when the plate is at 12 volts. Figs. 2 and 3 show similar results,

Fig. 2.

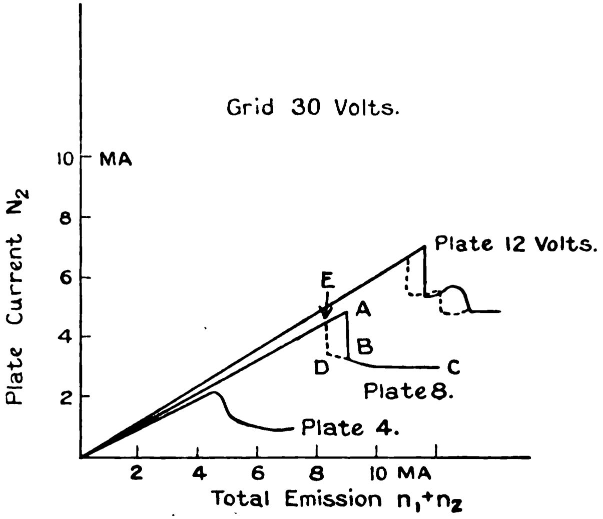
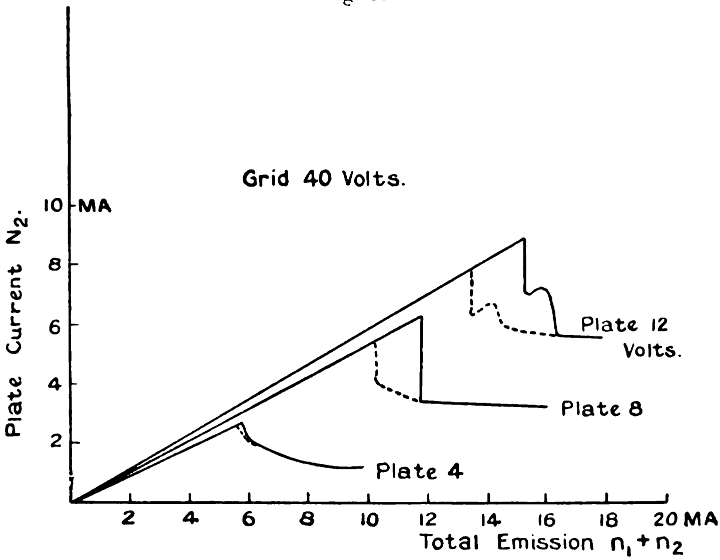


Fig. 3.



and indicate that the range of values of n_2 over which it is proportional to n_1+n_2 is increased if either the grid potential or the plate potential be increased.

If the total emission n_1+n_2 be increased beyond the range over which n_2 is proportional to n_1+n_2 in all cases the plate current n_2 decreases. If the plate and grid potentials are comparatively small, as in fig. 1, the decrease of n_2 with increasing n_1+n_2 is gradual, but for the higher values of grid and plate potential, as in some of the curves in figs. 2, 3, the fall is abrupt. For example in fig. 3, when the grid is at 40 volts and the plate at 8 volts, the largest plate current obtained is 6·4 milliamps. when the total emission is 11·7 milliamps. The slightest increase in the filament temperature causes the plate current to drop to 3·4 milliamps. for almost exactly the same total emission. The grid current of course rises abruptly by an equal amount.

If the total emission is further increased beyond the point where the drop in the plate current occurs the plate current remains low, though in one or two of the curves a small second maximum plate current is obtained for very high emissions.

The straight portions of the curves can be taken as giving a measure of the proportion of the electrons leaving the filament which pass through the grid, and therefore after the drop in the plate current occurs a large number of electrons which pass through the grid must fail to reach the plate and must return to the grid. An example will perhaps make this clearer. In the case in which the grid is at 40 and the plate at 8, the maximum plate current is 6·4 m.a., the filament emission being 11·7 m.a., that is $\frac{64}{117}$ of the electrons from the filament pass through the grid, the remainder being collected on the grid.

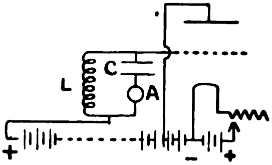
When the emission is 14 m.a. the current passing through the grid is therefore 7·7 m.a., but the curve shows that the plate current for this emission is only 3·3 m.a., and therefore more than half the electrons which passed through the grid must have been stopped before reaching the plate and have then returned to the grid.

There is one further important peculiarity of the curves to be mentioned, of which the curve for plate at 8 volts in fig. 2 is an example. In this curve if the emission is gradually raised the current increases up to point A, the sudden drop occurs to B, and further increase in emission takes it to C. If at this stage the emission is gradually reduced the curve will be retraced from C to B; at B, however, there is not an abrupt rise to A, but the curve from B to D is obtained, and the abrupt rise then occurs to E, after which the original curve is retraced. The curves for decreasing emission are all shown dotted where they deviate from the curves for increasing emission. It appears, therefore, that for certain values of the emission there may be two possible distributions of current in the valve.

The experimental facts therefore to be explained in the theory which will be given in section 4 are that if various currents from a source at zero potential are passed through a grid at potential V, the plate at potential V_0 (less than V), will receive the whole of this current if it is not larger than a certain critical value; only a proportion if it is above this value; while just below this critical value the plate can receive either the whole or only a proportion. The critical value depends on both V_0 and V.

3. A valve of this type can be used as a generator of continuous oscillations of either high or low frequency. It is only necessary to insert in the lead to the grid an oscillatory circuit as shown in fig. 4.

Fig. 4.



L is an inductance, C a capacity, and A a hot-wire milliammeter. If with the grid at, say, 40 volts and the plate at 8 volts the filament is gradually heated up, at the moment when the plate current experiences its sudden drop, oscillations will commence and be maintained in the oscillatory circuit, their presence being revealed by the hot-wire ammeter A. A similar result can be obtained for low frequency oscillations by inserting a telephone in place of the oscillatory circuit. The same heating of filament which caused high frequency oscillations will cause the telephone to emit a continuous hum showing that low frequency oscillations are being obtained.

The maintenance of these oscillations is independent of any electromagnetic or capacity coupling between the plate and grid. The method of maintenance can be seen from an inspection of figs. 2 and 3. If the plate is kept at 8 volts and the filament heated till the total emission is 9 milliamps., then if the grid potential is 30 volts, the plate current is 3·3 m.a., and the grid current is 9 − 3·3 = 5·7 m.a.

If the grid potential is increased to 40 volts the plate current is 5 m.a., and the grid current is therefore 4 m.a. Thus increasing the grid potential from 30 to 40 volts reduces the grid current from 5·7 to 4 m.a. A decrease of current for an increase of potential is an unstable condition—what is called a "negative resistance"—and in this state the valve is capable of maintaining oscillations.

Even if there are no oscillatory circuits in the leads it seems likely that short wave oscillations may arise in them or in the circuits of the milliammeters used for measuring the currents. The small kinks in the curves for the larger currents are probably due to this cause; the readings of the milliammeters in these regions being somewhat unsteady, as often occurs when intermittent oscillations are taking place.

4. The explanation of the preceding results is evidently to be looked for in the fact that the field between the electrodes is determined not only by the potentials of the electrodes, but also by the charge on the electrons which happen at any instant to be in the space between the electrodes. For simplicity the electrodes may be taken as parallel plates a distance d apart, kept at potentials V_0 and V_1. The distance x is measured from the plane which is at the potential V_0.

Let the current i per sq. cm. flow between the planes carried by electrons which started from a filament at zero potential. At the point x let V be the potential, v the velocity of the electrons, e their charge, m their mass, and let ρ be the charge per c.c. at x. The current is evidently independent of x, but V, v, and ρ are functions of x.

Then the general equations are:—

$$\left.\begin{aligned}\tfrac{1}{2}mv^2 &= eV\\ i &= \rho v\\ \frac{d^2V}{dx^2} &= 4\pi\rho\end{aligned}\right\}\text{(A)}.$$

Apparently no general solution of these equations has been published, but a special case was solved by Child[*]. He found that if $V_0=0$, *i. e.*, if the electrons start with zero velocity at one electrode, then the maximum current the other electrode could receive per cm. was proportional to $V^{3/2}/d^2$ and that the corresponding potential distribution between the plates was $V=V_1\left(\frac{x}{d}\right)^{4/3}$.

The reason this is the maximum possible current is that the corresponding distribution causes the electric force to be zero at the plane from which the electrons start.

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[*] Phys. Rev. 1911, p. 499.

If the supply of electrons is insufficient to maintain this maximum current then a smaller current will flow. The field due to the charged electrodes will still be distorted, but not to so great an extent.

The above results were extended by Langmuir * to cases of cylindrical electrodes and electrodes of any shape. He found the current was still proportional to the three-halves power of the potential difference.

If, instead of the electrons leaving the zero-potential plane and being accelerated up to the plane of potential V_1, which they reach with a velocity $\sqrt{\frac{2e}{m}V_1}$, we start them back from this plane with this velocity and let them run in the retarding field to the plate, the equations (A) are unaffected, i and v having changed sign; the boundary conditions are also the same, and therefore the maximum current which can just get across is the same as before, and the resulting potential distribution is the same.

The case we are dealing with is rather more complicated than this. Let the plane at potential V_0 represent the plate and that at V_1 the grid, the filament being taken as zero.

The electrons from the filament have the velocity $\sqrt{\frac{2e}{m}V_1}$ as they pass the grid, and they move in a retarding field up to the plate, but in all the experiments done V_0 was not zero but positive.

The boundary condition upon which the previous results were based, that in the limiting case the electric force just outside the electrode is zero, no longer holds, for the electrons hit the plate with a velocity $\sqrt{\frac{2e}{m}V_0}$, and will therefore reach it whatever the force at the plate. We must look elsewhere for a force which can limit the current reaching the plate.

The general equations have not been solved for this particular boundary condition, but it is easy to see what happens without attempting a solution. In fig. 5 let OA be equal to V_0, GB equal V_1, and OG be the distance between the plate and grid, then the ordinates of the straight line AB represent the potentials at the various points between the plate and grid when no current is flowing.

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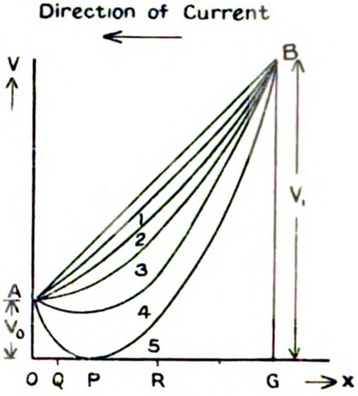
* Phys. Rev. 1913, p. 450.

Now suppose a small current passes the grid and flows to the plate, the electrons having velocity $\sqrt{\frac{2e}{m}V}$ at a place whose potential is V. The passage of this current affects the potential distribution, which becomes something like curve 1. If the current is increased the distortion of the field is more and we get curve 2, a larger current still will give 3, and so on with 4 and 5.

Fig. 5.



Distribution of Potential between plate at O and grid at A.

Curve 3 is drawn as that one of the family which is parallel to Ox at the plate, that is the electric force is zero at the plate. In curve 4 we get a reversal of the electric force between the electrodes, the electrons reach a minimum velocity at the place where the tangent is parallel to Ox, and then accelerate again till they reach the plate. Curve 5 is the limiting one. At P the electrons come momentarily to rest, the potential being zero and the force also zero, and then move on to the plate.

Curve 5 represents a state of affairs to which we can apply Child's results. If i is the current from grid to plate, then i satisfies the boundary conditions for maximum current between parallel planes distant apart OP charged to potentials V_0 and 0, and also for parallel planes distant apart PG charged to potentials V_1 and 0.

Hence $i=\frac{kV_0^{3/2}}{OP^2}=\frac{kV_1^{3/2}}{PG^2}$, k being a constant, from which both i and the position of P can be found in terms of V_0, V_1, and the distance between grid and plate.

The potential distributions can also be calculated :—

$$\text{To the right of P} \qquad V = V_1\left(\frac{x-\text{OP}}{\text{PG}}\right)^{4/3}.$$

$$\text{To the left of P} \qquad V = V_0\left(\frac{\text{OP}-x}{\text{OP}}\right)^{4/3}.$$

In all the curves 2 to 5 all the electrons passing the grid reach the plate, and the calculations just made determine the maximum current the plate can receive under these conditions. The question which next arises is, What happens if we force through the grid a current larger than this maximum? In the first place it is evident that the curve cannot sink below the x axis, for all the electrons would be brought to rest at the point nearest to G where the curve cuts the axis, and the force there would tend to send them back to the grid, none would reach the plate, and hence there would be no space-charge between this point and the plate, and the assumed distribution is therefore impossible.

The remaining possibilities are distribution curves which touch Ox at points other than P. We can at once rule out the possibility of such points being nearer to O than P, for if Q were the point of contact of one of the curves the plate current would be $\dfrac{kV_0^{3/2}}{\text{OQ}^2}$, and the current passing the grid would be $\dfrac{kV_1^{3/2}}{\text{GQ}^2}$, but $\dfrac{V_0^{3/2}}{V_1^{3/2}} = \dfrac{\text{OP}^2}{\text{PG}^2}$, and therefore the plate current would be larger than the current entering through the grid, which is impossible. We are reduced therefore to potential curves which touch Ox at points such as R to the right of of P. A calculation similar to that just made would show that to make $V=0$ at R, and also the force $\dfrac{dV}{dx}$ zero there, would require a larger current from the grid than the plate receives; this means that some of the electrons which come to rest at R must return to the grid, and therefore to the right of R we are dealing with space-charges due to both direct and return currents. It is necessary then to examine how equations (A) would be modified in such a case.

Let i be the current passing through the grid from the filament side, i_1 the current returning from R towards the grid. The balance $i-i_1$ goes on to the plate. Let ρ be the charge per c.c. at distance x due to current i and ρ_1 that due to current i_1.

Then the velocities of the electrons, whether coming or returning, is the same at the distance x, being given by

$$\left.\begin{array}{ll} & \frac{1}{2}mv^2=eV \\ \text{also} & i+i_1=(\rho+\rho_1)v \\ \text{and} & \frac{d^2V}{dx^2}=4\pi(\rho+\rho_1) \end{array}\right\} \text{(B)}.$$

These equations give exactly the same solution as (A) if $i+i_1$ replaces i, and we thus find that the current to the right of R is given by

$$i+i_1=\frac{kV_1^{3/2}}{RG^2} \quad \ldots\ldots\ldots \quad (1)$$

The current to the left of R is the current i_P reaching the plate:—

$$i_P=i-i_1 \quad \ldots\ldots\ldots \quad (2)$$

and

$$i_P=\frac{kV_0^{3/2}}{OR^2} \quad \ldots\ldots\ldots \quad (3)$$

From which i_P can be found in terms of i for given values of V_1 and V_0. It should be noted that the necessary condition that the stream of electrons entering through the grid should divide into two streams, one going on to the plate and the other returning to the grid, is that at some point both $V=0$ and $\frac{dV}{dx}=0$. For it is necessary that the electrons should come to rest, and in addition it is also necessary that at the place where they come to rest the electric force should be zero, as otherwise the stream would not divide there, since they would all start again in the direction of the force. Thus all the possible potential distributions for cases where all the incident electrons do not reach the plate must touch Ox somewhere between P and G.

The solution of equations 1, 2, 3 giving i_P in terms of i is a tedious business, and all the information required can be got more easily by working out the currents for different values of OR as below.

Take the special case grid at 40 volts and plate at 8 volts above the filament, the distance from plate to grid being 1 cm.

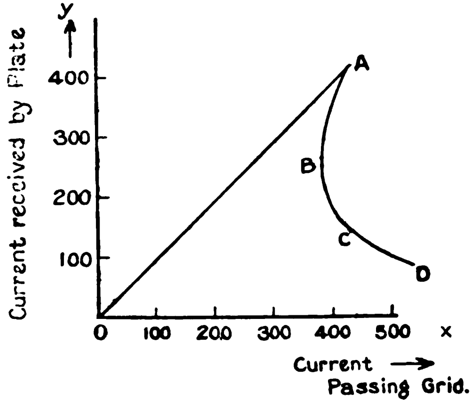
The maximum current which can reach the plate causes the potential to drop to zero at a distance OP$=\cdot 23$ cm. from the plate (calculated from $\frac{8^{3/2}}{OP^2}=\frac{40^{3/2}}{(1-OP)^2}$), and the magnitude of this current in arbitrary units is 426. Any current less than this can flow from the grid to the plate causing some such potential distribution as 1, 2, 3, or 4.

The currents for potential distributions which touch O*x* at R where OR is greater than ·23 are shown in the table following, *i* being the current entering through the grid and i_P the current reaching the plate.

OR.	*i*.	i_P.
·24	416	392
·25	406	360
·26	396	333
·27	391	309
·3	383	250
·35	393	178
·4	421	141
·45	466	112
·5	548	91

These results are shown graphically in fig. 6, the current entering through the grid being plotted along O*x*, and the

Fig. 6.



number reaching the plate along O*y*. The straight part of the curve corresponds to the currents which cross without any current returning to the grid, and the remainder of the curve comes from the table.

It is seen that currents up to about 380 coming through the grid go direct across to the plate; but for currents between 380 and 426 there is the rather unexpected result that there are three possibilities. As an example, if a current of 400 units is forced through the grid either (1) all the 400 units reach the plate, (2) 350 reach the plate and 50 return to the grid, or (3) 170 reach the plate and 230 return to the grid.

For currents larger than 426 there is only one possible plate current which decreases as the current forced through the grid increases.

If a similar calculation is performed when the plate is at 12 volts, the curve obtained is similar, but the straight portion is longer, the maximum plate current being larger than when the plate is at 8 volts.

5. It is easily seen that the method of conducting the experiments described can obtain from fig. 6 a curve like those actually obtained. The current passing through the grid from the filament is very fairly accurately proportional to the total current leaving the filament, and therefore, by an alteration of scale, fig. 6 will show plate current plotted against total emission. As the filament temperature is increased we move along OA, and will reach A unless the condition represented by the curve ABC is more stable than the last part of the straight line OA. At A a further increase of grid current can only take us to the portion CD, and there is therefore a sudden drop from A to C, after which the plate current decreases as the current from the grid increases.

When the return journey is made, decreasing the heating emission brings us a long DCB unless the state C to B is so unstable that the currents charge to distributions given by the curve BA or OA. At B a further decrease of emission gives no alternative except to return to OA, and a rapid rise occurs at B. The experiments show that OA is stable when traversed by gradually increasing the filament emission and CB is stable when traversed by retracing it. It is of interest that if we are near A on the portion OA and the batteries charging the plate or grid are momentarily disconnected and replaced the plate current sinks to the value given by the curve CB. The only method of getting from O to A is to keep the grid and plate batteries attached and increase the filament heating.

So far, except in one or two doubtful cases, it has not been possible to get the currents in a distribution corresponding to the portion BA of the curve.

6. There is thus a very fair agreement between the experimental and calculated curves, and what differences there are can be accounted for by the assumptions made in the theory.

The main differences are that the grid and plate were taken as parallel planes instead of coaxial cylinders, and the filament as an equipotential, whereas, in fact, there is down it the voltage drop of about 4 volts, due to the heating current. The theory also accounts for the fact that the maximum current which can reach the plate will be increased if either the plate potential or the grid potential is increased.

The reason for the non-occurence of the chief phenomena with the Mullard valve is that owing to the dimensions the maximum current which can pass to the plate for a certain potential of the grid (and any plate potential) is greater than the maximum current which can flow from the filament for that particular grid potential. It is therefore impossible to force through the grid more current than the grid-plate space can carry to the plate. The maximum current which can flow to the plate gets less as the distance between the grid and plate is increased, and if the plate diameter is about 3 times the diameter of the grid it becomes possible to pass through the grid more current than the space can carry, and the drop in the plate current will occur.

7. An interesting point arises with regard to secondary emission of electrons from the plate due to the impact of the primary ones. For any value of the current passing the grid greater than that which causes the potential distribution 3 in fig. 5, the force at the plate tends to take electrons back to it, and therefore for all these currents the usual effects due to secondary emission will be absent (unless there is an appreciable velocity of emission).

Another suggestive question is whether a potential distribution curve could touch the axis Ox at more than one point.

If there are only electrons present this is not possible, but if, in addition, there are positive ions present it could theoretically occur. The electrons would come momentarily to rest at the points where the curve touched the axis Ox, at which points the positives would have their maximum velocity while they would have their minimum velocity at intermediate positions where the electrons were moving fastest. It is probable that some such condition exists in the striated positive column.

I have to thank Professor Townsend very much for advice and criticism.

C. *The Absorption of Ultra-violet Light in Dilute Solutions. By* C. J. Webber Grieveson, *B.A., B.Sc., Formerly Demy of Magdalen College, Oxford* *.

Introduction.

1. IN his paper on the absorption of ultra-violet light in solutions (Phil. Mag. xvii. p. 710, May 1909), Dr. F. B. Pidduck gives an account of some experiments with solutions of common salt and potassium bromide in distilled water and with tap-water. According to his results about 1·5 parts of potassium bromide per million reduce the transparency of 15 mm. of distilled water by 25 per cent. If substances can be found which absorb very strongly in dilute solution, *e.g.*, about ten times as strongly as potassium bromide, it may be possible to use this absorption to measure very weak concentrations of these substances. It has been suggested that if a substance of this sort could be obtained, then in certain cases the volume-rate of flow of a river might be found by adding a quantity of the substance to the water at a certain place and noting the change of concentration further down. It was with the object of obtaining some information on this matter that the investigation summarized below was undertaken.

Apparatus and Method.

2. In general construction the apparatus follows the usual parallel plate form, arranged so that the U.V. light can fall on one of the plates, absorption being measured by the change in the photo-electric effect. But in order to compare absorptions more directly, this plate is divided into two equal parts, and to reach these parts the U.V. light has to pass through one or other of the quartz-bottomed vessels containing the liquids. The two plates—*i.e.* the two parts of the upper plate (P_1, P_2 in fig. 1)—are semi-circular, cut from one piece of brass and silver-plated. Each is mounted on two long ebonite pillars (not shown) and thus rigidly supported below the top plate (P) of the case. The common lower plate of the condenser consists of a silver-plated gauze (G) mounted on a stout metal ring supported by ebonite pillars. A suitable saturation potential difference between the plates is maintained by a battery of small accumulators. By using four brass pillars fitted with screw-heads instead of the usual

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* Communicated by Prof. J. S. Townsend, F.R.S.

three to support the top plate P, the latter can easily be turned through two right angles and the plates P_1, P_2 interchanged. The sides of the apparatus are screened by a cylindrical brass case hanging from the top plate. Fig. 1

Fig. 1.

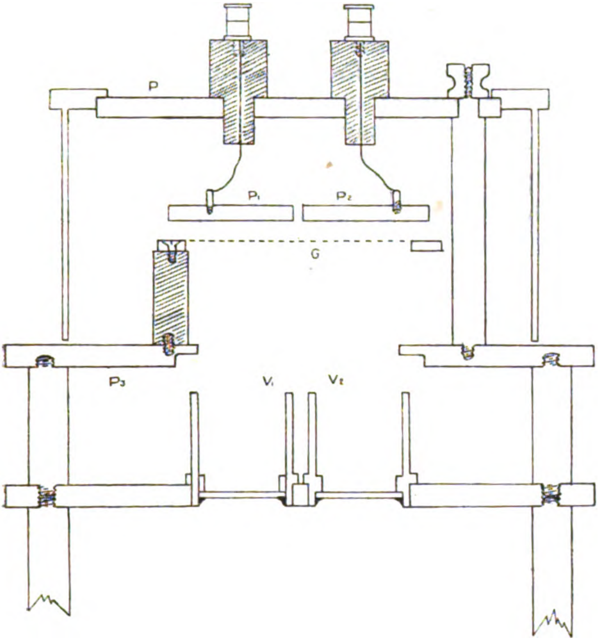


Diagram illustrating form of Plate Apparatus.

Dimensions.

Diameter of silver plates (P_1, P_2)	7·3 cm.
Distance of P_1 and P_2 below top plate P	2·5 cm.
Distance between P_1 and gauze G	0·7 cm.
Internal diameter of gauze-ring	6·4 cm.
Height of gauze G above plate P_3	2·8 cm.
Solution Vessels (V_1, V_2):	
Internal diameter	2·5 cm.
Overall height	3·1 cm.

Vessels centred at 3·1 cm. apart.

illustrates the construction of the apparatus, although it is not strictly a central section of it. Examples of the supporting pillars and ebonites are introduced slightly out of their true position to show the method of mounting adopted.

Over apertures near the centre of a stout brass plate some distance below the grating stand the two vessels V_1, V_2—cylindrical and with quartz bases—used to contain the solutions. The line joining their centres is perpendicular to the line of separation of the semicircular plates P_1, P_2, so that each vessel is directly under the middle of one of these plates. Ultra-violet light from a spark-gap parallel to the line of separation of the plates enters the vessels from below and passes up through the solutions to the plates above.

3. The photo-electric effect is measured by an electrometer and induction balance connected with the parallel plate apparatus by a special key (K, fig. 2). In parallel with the plates P_1, P_2 are the inner plates of two similar condensers C_1, C_2, whose outer plates may be raised to any desired potential by a battery connected through two potentiometers R_1, R_2 as shown in fig. 2; X is a small sliding rheostat used as a fine adjustment when necessary.

Fig. 2.

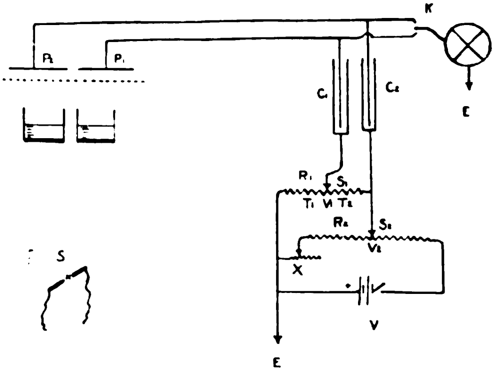


Diagram of Apparatus.

In performing the experiment the more transparent solution is put under the plate P_2, whose corresponding condenser C_2 is connected directly with the slider S_2 of the main potentiometer R_2. The spark is put on for a time and the electrometer is kept undeflected by adjusting S_2. Then K is switched over, connecting the electrometer with the other plate P_1. In general the electrometer is deflected, but if the ratio slider S_1 (on the potentiometer R_1) has been placed at the correct position to balance the charge on P_1, there is no movement. It follows from the theory of the system that if in this case q_1, q_2 are the charges acquired by the plates P_1, P_2, respectively, and if v_1, v_2 are the potentials of the sliders S_1, S_2, respectively, then

$$q_1 = c_1 v_1$$

$$\text{and} \qquad q_2 = c_2 v_2.$$

Also, if the resistances of the parts into which R_1 is divided by S_1 are r_1 and r_2, then

$$\frac{v_1}{v_2} = \frac{r_1}{(r_1 + r_2)}.$$

$$\text{Hence} \qquad \frac{q_1}{q_2} = \frac{c_1}{c_2} \cdot \frac{r_1}{(r_1 + r_2)}.$$

Replacing one of the solutions—the one under P_1—by a solution of another strength we get new values for q_1 and r_1 such that

$$\frac{q_1'}{q_2} = \frac{c_1}{c_2} \cdot \frac{r_1'}{(r_1 + r_2)}.$$

$$\text{and so} \qquad \frac{q_1'}{q_1} = \frac{r_1'}{r_1}.$$

Hence the position of the slider S_1 is a measure of the photo-electric effect and so of the transmitted light. It has been stated, however, by Griffith that the photo-electric effect (E) is not exactly proportional to the intensity (I) of the light but that E/I increases with I and at a gradually increasing rate. (For the reference see Pidduck's paper, *loc. cit.*) Subject to this proviso—which is disputed by other experimenters—the ratio $\frac{r_1'}{r_1}$ [for convenience referred to later as the transmission coefficient, μ] measures the relative transparency of the two liquids.

4. In general, the method of procedure was to take as the absorption standard a depth of 10 mm. of distilled water and to compare other liquids and depths with this. Before a specimen of a solution was examined both vessels were filled to a depth of 10 mm. with distilled water and the value r_1 of the ratio resistance was determined for no deflexion. The water in one of the vessels was then replaced by the same volume of the solution and the new value r_1' found. The water in the second vessel remained unchanged and formed a definite standard of comparison by which were eliminated errors arising from variations in the timing and the brilliance of the spark. To test this compensation the spark was purposely altered in length and intensity, and over a wide

range the consequent change in the reading was less than the general experimental error. In the experiments on the solutions care was taken to keep the spark working as steadily as possible.

Other errors liable to arise are those due to lack of uniformity of the solutions. These were very carefully made up and were kept in closely stoppered bottles. Even then one or two substances showed irregularity, the solutions tending to become more opaque with dilution. This was afterwards found to be due to traces of impurity. Substances which showed this effect invariably gave uncertain readings near these critical strengths. In the results recorded below only those substances are mentioned whose solutions gave readings that could be determined definitely.

To ensure constant electric conditions during measurement the spark was kept on just long enough for the slider to reach the same potentiometer division every time a reading was taken.

Solutions Tested and Results Obtained.

5. Among the substances examined was a series of some of the salts of sodium in order to compare the effects of the acid radicle on the absorption. Tap-water also was tested and the effect of adding a certain proportion of tap-water to distilled water solutions. Graphs of the change of the transmission coefficient (μ) of these solutions with concentration have been prepared, and it is by these curves that the results are most easily studied. In general form they are all similar (see fig. 3). Starting from the vertical axis at $\mu=1$ they fall more or less steeply at first but at a gradually decreasing rate until the gradient becomes very small and they approximate to straight lines slowly approaching the horizontal axis.

6. The chief results are as follows:—

Curve 1. *Sodium Chloride.* (Fig. 3.)

The curve for sodium chloride is quite even and regular. It falls steeply at first, but gradually the slope decreases until for strengths above $2{\cdot}5 \,.\, 10^{-3}$ N it reaches a practically constant value. Different specimens agreed within ½ per cent.

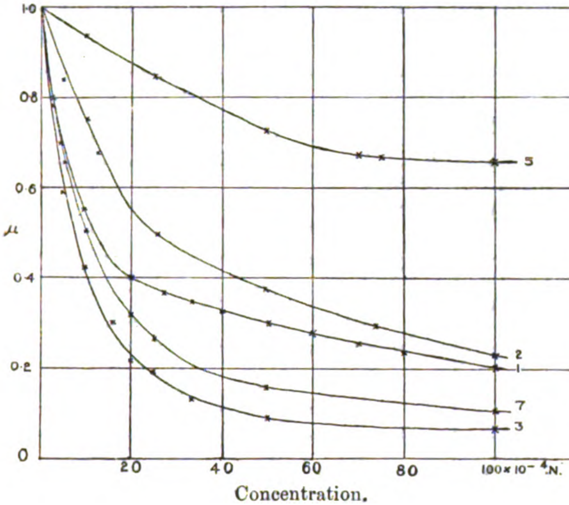
Curve 2. *Sodium Bicarbonate.* (Fig. 3.)

This curve does not fall quite as steeply as that for the chloride but it exhibits the same general form.

Curve 3. *Sodium Carbonate.* (Fig. 3.)

The normal carbonate absorbs much more readily in dilute solution than either the chloride or bicarbonate. The value of μ reaches 0·5 at a strength of about $6\cdot5 \,.\, 10^{-4}$ N (*i.e.* about 0·035 gm. per litre). For this absorption the chloride requires $1\cdot2 \,.\, 10^{-3}$ N (about 0·6 gm. per litre) and the bicarbonate $2\cdot6 \,.\, 10^{-3}$ N (about 0·22 gm. per litre). At the higher strengths the curve for the carbonate is noticeably flatter than the other two, so that concentrating beyond $5 \,.\, 10^{-3}$ N has comparatively little effect.

Fig. 3.—Substances in Table I.



Curve 4. *Sodium Diphosphate.* (Fig. 4.)

This curve falls even more steeply than curve 3 and it falls much lower before flattening out. The presence of 0·04 gm. per litre (about $2\cdot3 \,.\, 10^{-4}$ N) reduces μ to 0·5, and the presence of 0·3 gm. per litre reduces it to 0·02.

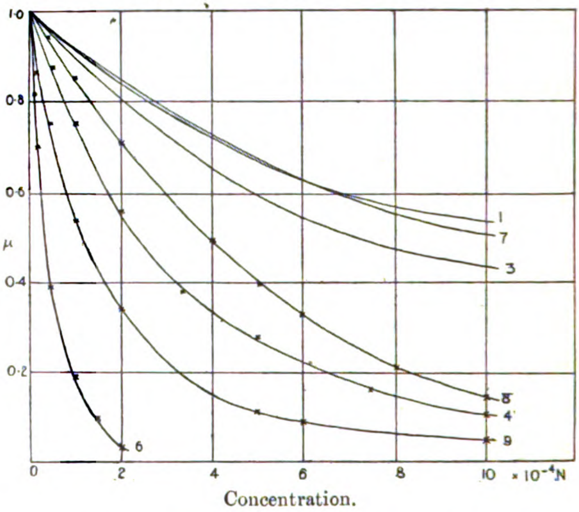
Curve 5. *Sodium Sulphate.* (Fig. 3.)

Sodium sulphate solution is remarkably transparent to the light from a zinc spark-gap. Even a centinormal solution does not reduce the photo-electric effect by one half, and further concentration would appear to have little effect for at 10^{-2} N the curve is almost horizontal.

Curve 6. *Sodium Nitrate.* (Figs. 4 & 5.)

As an absorber sodium nitrate is the most efficient of all the sodium salts examined. A concentration of $4 . 10^{-5}$ N absorbs half the effective light, and 10 mm. of a solution of strength $20 . 10^{-5}$ N is nearly opaque. This remarkably rapid fall in the curve was found with all the nitrates examined. In spite of the low concentration (from 1 to 10 parts per million) the individual readings all lie closely to the curve; the greatest divergence from the mean at any strength was not more than $\frac{1}{2}$ per cent. In fig. 5 this curve is shown dotted.

Fig. 4.—Substances in Table II.



Curve 7. *Manganese Chloride.* (Fig. 3.)

At some of the lower concentrations solutions of this substance gave somewhat uncertain readings at first. The curve reaches $\mu = 0{\cdot}5$ at a strength of about 10^{-3} N.

As the curves for sodium chloride and carbonate and for manganese chloride (curves 1, 7, 3) overlap rather closely at the higher end in fig. 3 they are shown enlarged in fig. 4, which is on a larger scale.

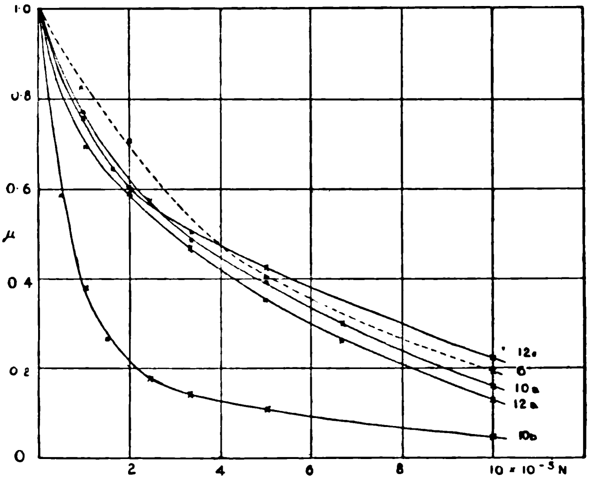
Curve 8. *Copper Sulphate.* (Fig. 4.)

Of the salts of copper so far examined the sulphate gives the most consistent results. The nitrate absorbs much more strongly, but it is less certain in its action. The curve for the sulphate falls quite steadily, passing $\mu = 0{\cdot}5$ at a strength of about $3{\cdot}5 \,.\, 10^{-4}$ N (*i. e.* about 0·03 gm. [anhydrous] per litre) and reaching $\mu = 0{\cdot}14$ at 10^{-3} N.

Curve 9. *Potassium Permanganate.* (Fig. 4.)

Potassium permanganate solutions absorb readily. A strength of 10^{-4} N is sufficient to reduce μ by nearly one-half and 10^{-3} N brings it down to one-twentieth. The very weak solutions (below 3 parts per million) showed a slight tendency to become more transparent on exposure to the air. The values given in Table II. are those found for the specimens as soon as they were put into the apparatus.

Fig. 5.—Nitrates (Table III.).



Curve 10. *Calcium Nitrate.* (Fig. 5.)

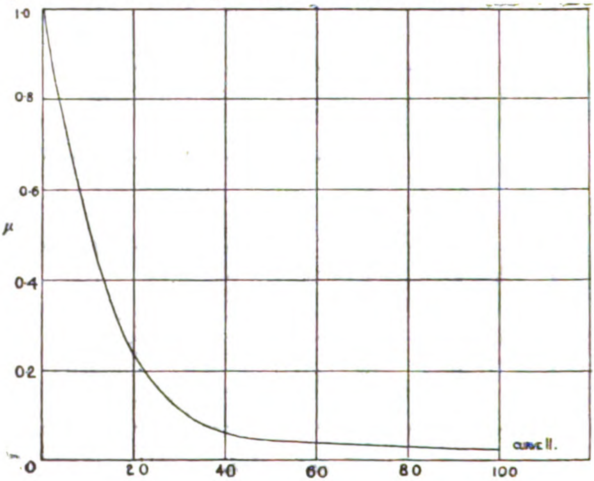
This like the other nitrates was found to absorb strongly. A solution stronger than $2 \,.\, 10^{-4}$ N is nearly opaque. The readings given by the individual specimens agreed well among themselves and gave mean values lying very closely to the curve.

The effect of increasing the thickness of the solution to 20 mm. is illustrated in the position of curve 10 *b*, which compares the absorption of 20 mm. of calcium nitrate solution with that of 20 mm. of distilled water. As would be expected this curve falls considerably below curve 10 *a*—the curve for a depth of 10 mm.—and μ reaches 0·5 at a strength below 10^{-5} N and $\mu = 0 \cdot 1$ at about $5 \,.\, 10^{-5}$ N. The individual points lie accurately on the curve although it falls so steeply.

Curve 11. *Tap Water.* (Fig. 6.)

Early in the course of the experiments it was found that 10 mm. of Oxford tap-water was practically opaque to the U.V. light from the spark-gap. If, then, solutions in tap-water were to be examined it was evident that only mixtures of tap-water and distilled water could be used as solvents, or else the spark would have to be made much more powerful. As the latter alternative would upset the continuity of the experiments a curve for mixtures of tap-water (filtered) and distilled water was taken off and some solutions in one or two of these mixtures were examined. Later the spark was slightly intensified also.

Fig. 6.—Mixtures of tap-water and distilled water (Table IV.).



Percentage of tap-water in mixture.

As tap-water is a mixture of dilute solutions of various substances, it is to be expected that mixtures of tap-water and distilled water would give a series of points on a curve similar to those already obtained. The curve found falls remarkably steeply and reaches $\mu = 0 \cdot 5$ with only 10 per cent. of tap-water in the mixture. For a 50 per cent. mixture $\mu = 0 \cdot 04$. Since Oxford tap-water has only about 0·3 gm. of dissolved substance per litre, it is evident that small quantities of a few different substances in solution make a very opaque screen for ultra-violet light.

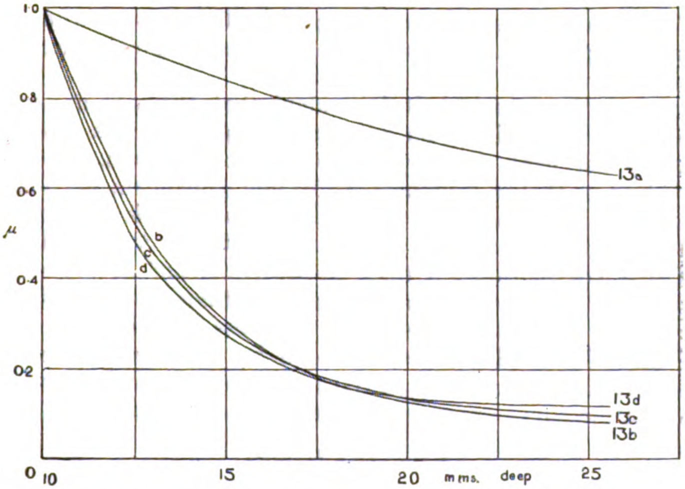
Curve 12. *Calcium Nitrate in Tap-Water Mixtures.* (Fig. 5.)

To examine to some extent the effect of the presence of other substances in the solution three separate series of readings were taken with solutions of calcium nitrate in mixtures of tap-water and distilled water. The mixtures used contained 10, 20, and 50 per cent. of tap-water respectively, and in each case the standard of comparison was 10 mm. depth of the mixture. In diluting these solutions it was arranged that the concentration of tap-water salts should remain constant throughout each series while the concentration of calcium nitrate was reduced.

All the curves obtained (curves 12 *a*, *b*, *c*) fall rather more steeply at first than the corresponding curve for solutions in distilled water (curve 10 *a*). The curves for the 10 and 20 per cent. mixtures are scarcely distinguishable at the weaker end, but increasing the proportion of tap-water to 50 per cent. of the dissolving mixture makes an appreciable difference. In fig. 5 curve 12 *b* is omitted for the sake of clearness.

Curves 13 *a*, *b*, *c*, *d*. *Effect of Thickness on Absorption.* (Fig. 7.)

Fig. 7.—Transmission and Depth (Table V.)



The last phenomenon to be examined was the change in the absorption due to increasing the depth of the solution. The absorption of 10 mm. of each liquid was taken as unity and with it were compared the absorptions of other depths.

Curves were drawn for distilled water (13 *a*), the 50 per cent. mixture of tap-water and distilled water (13 *b*), and solutions of calcium nitrate of strengths 10^{-5} N and $4 . 10^{-5}$ N in this 50 per cent. mixture (13 *c*, 13 *d*).

(a) *Distilled water.*

(b), (c), (d) *The* 50 *per cent. mixture and solutions in it.*

From the readings it is clear that the change of transmission with depth depends to some extent on the strength of the solution, although the general form of the curve remains the same. (The form of course varies to some extent with the particular solution.) It falls rapidly at first as the depth increases from 10 to 20 mm., but further increase in the depth produces comparatively little change. This, of course, agrees with the idea of selective absorption, and evidently a thickness of 20 or 30 mm. of tap-water would stop practically all the absorbable rays. The addition of small quantities of solute (in the particular case examined, calcium nitrate) to the tap-water, while reducing the actual transparency, made but little difference to the change of transparency with thickness. Each time the solution was strengthened the initial gradient became slightly steeper and at the same time the fraction absorbed in the last half centimetre was diminished. That is to say, in the stronger solutions more of the absorbable rays are stopped in the first centimetre and a proportionately smaller effect is produced by increasing the thickness.

From these curves it is evident that there is a depth beyond which it is of no advantage to go. In the case of the 50 per cent. mixture a thickness of 20 mm. absorbs much more than a thickness of 10 mm., but little is gained by increasing the depth beyond 20 mm. This maximum suitable depth depends on the strength of the solution. With a weaker solution than the equivalent of 50 per cent. tap-water it would naturally be greater than 20 mm. With a stronger solution it might be much less. As the strength of the solution decreases the bend in the curve becomes less pronounced and the initial gradient becomes less steep, so that the curve approaches that for distilled water (13 *a*).

Numerical Results.

7. The chief numerical results obtained in the course of the experiment are indicated in the following tables. In Tables I., II., and III. the first column indicates the concentration of the solutions in terms of 10^{-4} N or 10^{-5} N. The

other columns give the values obtained for the transmission coefficient, (μ), of these solutions at the various concentrations tested. In Tables I. and II. the value of μ is relative to the transmission of 10 mm. of distilled water.

In Table III. are grouped together the results obtained with solutions of calcium nitrate. The first column indicates the concentration in terms of 10^{-5} N. Columns 2 and 3 of the table give the values of the transmission coefficient for solutions in distilled water, column 2 being those for 10 mm. of solution relative to 10 mm. of distilled water, and column 3 those for 20 mm. of solution relative to 20 mm. of distilled water. The last three columns of Table III. show the values of μ obtained with solutions of calcium nitrate in mixtures of tap-water and distilled water. In column 4 the nitrate solutions were made up in a mixture of one of tap-water to nine of distilled water (known as the 10 per cent. mixture) and 10 mm. of this mixture was used as standard. In the dissolving mixtures used to obtain the figures in columns 5 and 6 the tap-water and distilled water were in the ratios 1 : 4 (the 20 per cent. mixture) and 1 : 1 (the 50 per cent. mixture) respectively. A depth of 10 mm. of the dissolving mixture was used as standard in each case, and the values of μ recorded are relative to the transmission of these standards.

Table IV. gives the values of μ obtained with mixtures of distilled water and tap-water (10 mm. deep), using 10 mm. of distilled water as the standard. Table V. illustrates the change in μ with change in depth of the solution. Four

TABLE I.

Transmission Coefficients of Solutions in Distilled Water. (*v.* Fig. 3.)

Concn. in 10^{-4} N.	Sodium Chloride. Curve 1.	Sodium Bicarbonate. Curve 2.	Sodium Carbonate. Curve 3.	Sodium Sulphate. Curve 5.	Manganese Chloride. Curve 7.
100	·202	·228	·068	·656	·101
50	·304	·375	·09	·727	·160
25	·383	·505	·194	·872	·265
10	·536	·765	·43	·945	·50
5	·670	·84	·591	—	·694
2·5	·801	—	·78	—	·81
0	1·0	1·0	1·0	1·0	1·0

examples are given: (i.) Distilled water; (ii.) A mixture of tap-water and distilled water in equal proportions (the 50 per cent. mixture); (iii.) & (iv.) Solutions of calcium nitrate of strengths 10^{-5} N and $4 . 10^{-5}$ N respectively in this 50 per cent. mixture.

In figs. 3 to 6 are given the curves corresponding with the tables.

TABLE II.

Transmission Coefficients of Solutions in Distilled Water. (*v.* Fig. 4.)

Concn. in 10^{-5} N.	Sodium Diphosphate. Curve 4.	Sodium Nitrate. Curve 6.	Copper Sulphate. Curve 8.	Potassium Permanganate. Curve 9.
100	·108	·018	·141	·052
50	·280	—	·398	·11
20	·571	·034	·71	·34
10	·756	·196	·874	·546
5	·871	·39	·95	·76
2	—	·701	·97	·87
0	1·0	1·0	1·0	1·0

TABLE III.

Transmission Coefficients of Calcium Nitrate Solutions. (*v.* Fig. 5.)

Concn. in 10^{-5} N.	In distilled water.		In the 10 per cent. mixture.	In the 20 per cent. mixture.	In the 50 per cent. mixture.
	Depth 10 mm. Curve 10 *a*.	Depth 20 mm. Curve 10 *b*.	Curve 12 *a*.	Curve 12 *b*.	Curve 12 *c*.
20	·040	—	·037	·04	·11
10	·16	·047	·133	·15	·22
5	·405	·105	·36	·3	·43
3·33	·48	·139	·483	·45	·505
2·5	·57	·179	—	—	—
2·0	—	—	·594	·59	·60
1	·77	·380*	·689	·76	·74
0	1·0	1·0	1·0	1·0	1·0

* At concentration $0{\cdot}5 . 10^{-5}$ N, $\mu = {\cdot}589$.

TABLE IV.

Transmission Coefficients of Mixtures of Tap Water and Distilled Water. (*v.* Fig. 6.)

Percentage of Tap Water in the mixture.	Curve 11.
100 %	·021
50	·035
33·3	·089
20	·23
10	·504
5	·697
2	·85
0	1·0

TABLE V.

Change of Transmission Coefficient with Depth. (*v.* Fig. 7.)

Depth in mm.	Distilled Water. Curve 13*a*.	50 per cent. mixture of tap-water and distilled water. Curve 13*b*.	Solution 10^{-5} N of calcium nitrate in 50 per cent. mixture. Curve 13*c*.	Solution 4.10^{-5} N of calcium nitrate in 50 per cent. mixture. Curve 13*d*.
10	1·0	1·0	1·0	1·0
12·5	—	·547	·520	·478
15	·835	·304	·300	·277
20	·715	·124	·131	·135
25	·636	·085	·093	·117

In connexion with these results there is this to be said. The construction and dimensions of the apparatus naturally determine to a large extent the wave-lengths of the effective ultra-violet light. The light was not examined spectroscopically, but probably the wave-lengths present were chiefly the longer waves in the ultra-violet spectrum of zinc. A metal spark-gap in parallel with a condenser gives mainly the spectrum of the metal. Also, since in the actual apparatus the light had to pass through 10 cm. of air, 2 mm.

of quartz, 10 mm. of water or solution, and a further 6 cm. of air before reaching the silver plates, it is evident that only the longer waves could have got through to be effective. The fact that these wave-lengths occur in an absorption band of nitrate solutions determined the remarkable efficacy of the latter as absorbers.

Summary and Conclusion.

1. An apparatus is sketched and a method outlined by which the relation between the concentration of dilute solutions and their absorption of the ultra-violet light from a spark-gap may be studied.

2. Records are given of experiments with various substances in solution in distilled water, and curves are shown connecting the photo-electric effect of the transmitted light with the concentration. The effect of adding certain proportions of tap-water is also investigated.

It is shown that, in general, nitrates absorb more readily than some other substances, less than one part per million being sufficient to cause a measurable absorption in a depth of 10 mm. of solution. Of the other sodium salts examined, the phosphate and carbonate absorb fairly well, the chloride and bicarbonate require much stronger solutions to produce measurable effects, and the sulphate absorbs scarcely at all.

3. Finally, the relation between absorption and thickness of solution is examined in a few cases.

In conclusion, I should like to record my thanks to Professor Townsend, in whose laboratory the research was performed, for his kindly advice and encouragement during the course of the experiments.

CI. *Note on the Law of Force within the Atom.* *By* GEORGE GREEN, *D.Sc., Lecturer in Natural Philosophy in the University of Glasgow* [*].

X-RAY experimental investigation establishes very definite arrangements of atoms and atomic groups in crystalline and solid matter. According to modern ideas regarding matter, the mutual forces acting between atoms, which determine the equilibrium arrangements of atoms to form a crystal, are such as would arise when atoms act upon neighbouring atoms or electrons only in virtue of the forces

[*] Communicated by the Author.

depending on their electrical charges. By consideration of the conditions required for equilibrium of a homogeneous assemblage composed of positive and negative charges, it can, however, be shown that the inverse square law of attractive force between a positive charge and an electron cannot hold without modification when atomic distances between charges are reached. The inverse square law of attraction must give place to some law of repulsion between a positive and a negative charge, in order that the individual positive and negative charges may be able to retain the relative positions assigned to them in the experimentally determined space-lattice arrangement. Sir J. J. Thomson, in his recent papers [*] dealing with the subject of the electron theory of solids, assumes that the law of force between a positive charge e and an electron e is represented by

$$f=\frac{e^2}{r^2}-\frac{ce^2}{r^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c is a constant, and where the repulsive force ce^2/r^3 is supposed to come into operation only at atomic distances. No particular reason is stated in these papers for giving preference to the inverse cube law as the law of repulsive force just outside a positively-charged atom, although reference is made to the inverse cube law in an earlier paper [†]. The results arrived at by means of the law (1) given above prove that any indication of the correct form of the law of repulsion between a positive atom and an electron within atomic range would be of importance in establishing more satisfactorily the foundation of the electron theory of solids.

On the other hand, according to Bohr's theory of the atom, the inverse square law of attraction holds for the orbits of an electron within an atom, and also, according to α-ray experimental results obtained by Rutherford and others, the same law holds at distances within the innermost orbits of Bohr's theory.

The object of the present note is to indicate what seems to be a probable form of the law of force between a positive charge and an electron within atomic distances. With a law of force of the type under discussion below, it will appear that it is possible to harmonize the apparently opposite views referred to above, and in this way to obtain a link connecting two distinct fields of investigation.

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[*] Phil. Mag. xliii. p. 721; xliv. p. 657 (1922).

[†] Phil. Mag. xx. p. 239 (1910).

If we take ρ to represent a radius drawn from the centre of an atom, such that for all distances exceeding a small multiple of ρ the inverse square law of attraction holds, the law of force to be discussed below is of the type *

$$f=\frac{e^2}{r^2}\cos\frac{\rho}{r}\,; \quad \text{or} \quad f=\frac{e^2}{r^2}\cos\frac{\rho}{r}+\frac{ae^2}{r^n}\cos\frac{\rho}{r}+\frac{be^2}{r^n}\sin\frac{\rho}{r}. \quad (2)$$

Additional terms such as $\epsilon^{-\rho/r}$ may be included to represent a force ultimately falling to zero as r is diminished, but these do not immediately concern us. The particular case

$$f=\left(\frac{e^2}{r^2}+\frac{ae^2}{r^4}\right)\cos\frac{\rho}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is worthy of study, even as as illustrative system only, f being positive for attraction and negative for repulsion.

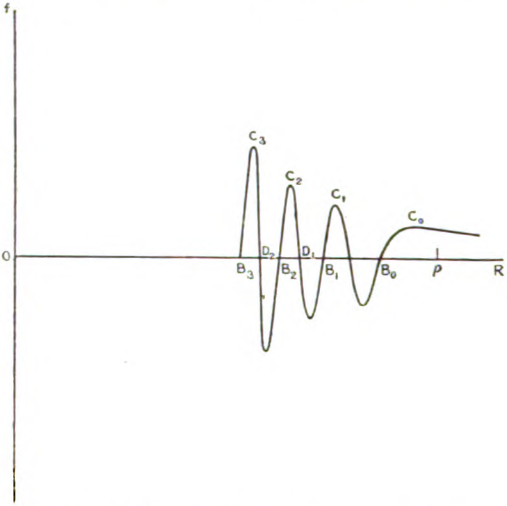

Diagram showing the force acting on an electron.

The force varies with r in the manner indicated in the diagram, where B_0, B_1, B_2, etc. represent positions within the atom at which an electron could remain at rest in stable equilibrium. These positions of equilibrium for an electron at rest correspond to values of r given by

$$\frac{\rho}{r_n}=(2n+\tfrac{1}{2})\pi\,; \quad n=0,\,1,\,2,\,3,\,\text{etc.} \quad . \quad . \quad (4)$$

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* A similar law of force was discussed from quite a different standpoint by Sir J. J. Thomson in Phil. Mag. xxxvii. p. 419 (1919).

Similarly, maxima of the attractive force on an electron occur at the positions defined by

$$\frac{\rho}{r}=2n\pi,\quad n=1,\ 2,\ 3,\ 4,\ \text{etc.},\ \ldots\ldots \qquad (5)$$

and represented by the points C_1, C_2, C_3, etc. in the diagram.

Consider now a slight radial displacement to be given to an electron initially at rest in one of the positions of equilibrium B_n. The restoring force corresponding to a displacement u is given by

$$F=\frac{e^2\rho}{r_n^4}\left(1+\frac{a}{r_n^2}\right)u.\ \ldots\ldots \qquad (6)$$

If m be the mass of an electron, the frequency ν of its vibration about the position B_n is accordingly given by

$$\nu^2=\frac{e^2\pi^4}{m\rho^3}\left\{(2n+\tfrac{1}{2})^4+\frac{\nu}{\rho^2}(2n+\tfrac{1}{2})^6\pi^2\right\},\ \ldots \qquad (7)$$

or, if a be an exceedingly small quantity, by

$$\nu=\frac{e\pi^2}{(m\rho^3)^{\frac{1}{2}}}\cdot(2n+\tfrac{1}{2})^2.\ \ldots\ldots \qquad (8)$$

The amount of work which must be expended in order to remove an electron from one of its equilibrium positions B_n to another B_p $(n > p)$ is represented by

$$W_n-W_p=\frac{e^2}{\rho}\int_{r_n}^{r_p}\left(\frac{\rho}{r^2}+\frac{a\rho}{r^4}\right)\cos\frac{\rho}{r}\,dr$$

$$=\frac{ae^2\pi^2}{\rho^3}\left\{(2n+\tfrac{1}{2})^2-(2p+\tfrac{1}{2})^2\right\},\ . \qquad (9)$$

an expression which is seen to depend only on the second term contained in the assumed law of force (3). The value of W_n alone, which represents the work required to remove an electron from position B_n to a position at rest at infinite distance, is

$$W_n=\frac{e^2}{\rho}+\frac{ae^2\pi^2}{\rho^3}(2n+\tfrac{1}{2})^2-\frac{2ae^2}{\rho^3},\ \ldots \qquad (10)$$

and the corresponding expression for the position C_n at which the attractive force is a maximum is

$$W_n=\frac{2ae^2}{\rho^3}n.\ \ldots\ldots \qquad (11)$$

The value of $W_n - W_p$ which we have obtained above represents also the amount of energy radiated corresponding to a change in the position of the electron from one equilibrium position to another. It is of interest to note that the expression is in harmony with a quantum theory, and the diagram on p. 1022 indicates clearly the manner in which energy would be radiated when an electron is in motion radially to or from the positive nucleus. If an electron originally at B_n receives just sufficient energy to allow it to reach the point D_n, it will then oscillate about the position B_{n+1}, and in so doing lose its energy gradually in waves which are of one definite frequency. If the electron were disturbed from B_n so as to reach D_n with a high inward velocity, it would then traverse a large range of r including many equilibrium positions before reaching the position at which it would ultimately settle after a series of diminishing oscillations. Taking the loss of energy by radiation proportional to the square of the acceleration at each instant, we see that the rate of loss would be very rapid so long as the inward radial motion continues. Each separate wave-length of the radiated energy would correspond with the movement of the electron from one of the equilibrium positions to the next—a distance which gradually diminishes as the inner positions are approached. The mean velocity of the electron between successive equilibrium positions likewise falls off during the inward motion, so that the energy radiation tends to be approximately of a uniform wave-length, as we may readily verify analytically. The frequency of the emitted radiation clearly depends on the initial energy of the inward motion, and this determines also the final position to which the electron would attain before coming to rest. We see therefore that the law of force under consideration provides a system in which energy would be radiated according to change of position of an electron within an atom in a manner in close conformity with the conditions of radiation loss postulated for a change of orbit of an electron on Bohr's theory of the atom.

So far we have retained the term ae^2/r^4 in the expression for the law of force; but in considering orbital motion of an electron round a positive nucleus, we can without loss limit the discussion to the simpler case where

$$f = \frac{e^2}{r^2} \cos \frac{\rho}{r} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

This force is attractive within each range of r from

$$\frac{\rho}{r} = (2n + \tfrac{1}{2})\pi \quad \text{to} \quad \frac{\rho}{r} = (2n - \tfrac{1}{2})\pi \, ;$$

and accordingly it might appear to be possible for an electron to revolve steadily at any distance r_0 within the range with angular velocity ω, provided

$$m\omega^2 r_0 = \frac{e^2}{r_0^2}\cos\frac{\rho}{r_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

To test the stability of such an orbital motion, we may assume that the electron is disturbed slightly from its circular path by a radial force, so that in the subsequent motion the angular momentum of the electron remains constant. The equation representing the subsequent radial motion is

$$m(\ddot{r} - r\dot{\theta}^2) = -\frac{e^2}{r^2}\cos\frac{\rho}{r}. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

When we take account of the condition of uniform angular momentum, replace r by $r_0 + z$, and retain only the terms depending on the first power of z, the above equation becomes

$$\ddot{z} + \omega^2\left(1 + \frac{2y^2}{\rho}\tan y\right)z = 0, \quad \text{where } y = \frac{\rho}{r_0}. \quad . \quad . \quad (15)$$

Hence a uniform orbital motion of the electron is stable, provided

$$\left(1 + \frac{2y^2}{\rho}\tan y\right) > 0\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

that is, when $\tan y$ is positive, and also when $\tan y$ is negative but not greater than $\rho/2y^2$. Thus in each range of r from one of the equilibrium positions B_n to the neighbouring position of maximum force C_n, and to a small distance beyond C_n only, the assumed orbital motion is stable. An electron describing an orbit near any one of the positions defined by $\rho/r = 2n\pi$, C_n, and subject to only a slight loss by radiation, would experience an exceedingly slow change of position towards B_n, because the loss of energy by radiation only affects the kinetic energy of the electron very slightly near C_n. In this neighbourhood the work done by the attraction of the positive charge upon an electron for any slight movement of the electron towards the nucleus has a maximum value ; and this work energy has to be expended before the electron sensibly changes its position. Accordingly, it is clear that the orbital motions of an electron corresponding to any one of the positions indicated by C_n, C_{n+1}, etc., once established, would be nearly permanent, provided the natural radiation loss was small.

They would therefore resemble closely the electron orbits postulated by Bohr.

Consider now the values of the kinetic energy, angular momentum, etc., of an electron revolving about a nucleus in one of these orbits corresponding to the position $\rho/r_n = 2n\pi$. In this orbit, with the usual notation, we have $m\omega^2 r_n = e^2/r_n^2$, and the kinetic energy of the electron is therefore $e^2/2r_n$ or $\frac{1}{2}m\omega^2 r_n^2$. Hence, in removing an electron from the orbit r_n to a position at rest at an infinite distance, an amount of energy T_n would be obtained, where $T_n = e^2/2r_n$. The loss of energy involved in a change of orbit of the electron from orbit r_n to r_p would be represented by

$$T_n - T_p = \frac{1}{2}\left(\frac{e^2}{r_n} - \frac{e^2}{r_p}\right), \quad . \quad . \quad . \quad . \quad (17)$$

or, since $r_n = \rho/2\pi n$, $r_p = \rho/2\pi p$, by

$$T_n - T_p = \frac{\pi e^2}{\rho}(n-p). \quad . \quad . \quad . \quad . \quad (18)$$

Similarly, the angular momentum of the electron in orbit r_n is easily shown to be given by A_n, where

$$A_n = (me^2 r_n)^{\frac{1}{2}} = \left(\frac{me^2\rho}{2\pi n}\right)^{\frac{1}{2}}, \quad . \quad . \quad . \quad (19)$$

and the change of angular momentum of the electron from orbit r_n to orbit r_p is accordingly

$$A_n - A_p = \left(\frac{me^2\rho}{2\pi}\right)^{\frac{1}{2}}\left\{\frac{1}{n^{\frac{1}{2}}} - \frac{1}{p^{\frac{1}{2}}}\right\}. \quad . \quad . \quad . \quad (20)$$

When we take n to represent some exceedingly large number, while the difference $n-p$ is small in comparison, the above expression for the change of angular momentum becomes

$$A_n - A_p = \left(\frac{me^2\rho}{8r_n^3}\right)^{\frac{1}{2}} \cdot (n-p). \quad . \quad . \quad . \quad (21)$$

This form indicates that the change of angular momentum of an electron from each orbit to the next is sensibly uniform for a very large number of orbits on either side of orbit n.

Keeping n to represent some very large but definite number, let us now choose a succession of orbits corresponding to the positions C_n defined by the indices

$n, \frac{n}{4}, \frac{n}{9}, \frac{n}{16}, \frac{n}{25}$, etc. The energy of the electron corresponding to these orbits is proportional to the numbers $1, \frac{1}{2^2}, \frac{1}{3^2}, \frac{1}{4^2}, \frac{1}{5^2}$, etc., respectively; the radii of these orbits are proportional to the numbers 1^2, 2^2, 3^2, 4^2, 5^2, etc., respectively; and the angular momenta are proportional to the numbers 1, 2, 3, 4, 5, etc., respectively. Hence these particular orbits can be identified with the system of orbits referred to in Bohr's theory of the atom. If we choose the constant n so that

$$2\pi A_n = 2\pi\left(\frac{me^2\rho}{2\pi n}\right)^{\frac{1}{2}} = h, \quad . \quad . \quad . \quad . \quad (22)$$

where h is Planck's constant, the above system of orbits coincides with that of Bohr, and leads to the same value for the Rydberg constant, namely $2\pi^2e^4m/h^3$. The particular law of force now under discussion does not provide any reason why the group of orbits referred to in the preceding paragraph should be of more importance in the atom than the intermediate orbits. But it is clear that this can be secured by a proper summation of terms of the same type.

The properties of the atomic system which we have been discussing are also interesting in relation to the manner in which radiation would take place from such a system, which we have already referred to in connexion with change of position of an electron from one equilibrium position to another. Similar results regarding the frequency of energy radiated are obtained in the case of a change of orbit of the electron as in the former case. The peculiar feature of the orbital motion at any position C_n is that, while the motion is stable for exceedingly small disturbances, the range of stability is small especially for the inner orbits, as we see from equation (16) above. When a disturbance occurs sufficient to render $\tan y$ negative and greater than $\rho/2y^2$, the orbital motion becomes unstable. The electron would then begin to move outwards with at first a gradual increase in the radial velocity, and then a rapidly increasing radial velocity when the force acting on it becomes repulsive. According to the law (12), the kinetic energy acquired by the electron in any range of r for which the force is repulsive is exactly equal to the amount required to enable it to surmount the succeeding range in which the force is attractive, loss of energy by radiation being neglected.

Through loss of energy the outward movement of the electron might come to an end in one of the outer orbits, but with a moderately large initial disturbance the electron would escape from the positive nucleus altogether. In the case where a disturbed electron is retained in one of the outer orbits, the outward movement would be brought to an end suddenly through loss of energy, and the train of waves radiated would be practically of a uniform wave-length, as in the case already referred to on p. 1024 above. The same explanation applies to the case of an electron acquiring suddenly an increase of angular momentum. It must move outwards, with loss of energy by radiation in each successive range of positive or negative force, until it reaches an orbit corresponding to the angular momentum which it now possesses. The outward movement would begin suddenly and come to an end suddenly, and the mean frequency of the train of waves radiated would be completely determined by the initial and final orbits of the electron.

As already stated, with relatively small loss of energy by radiation an electron might readily escape from the nucleus, carrying with it the bulk of the energy belonging to the orbit from which it set out. The relation of such an action of expulsion of an electron to the photo-electric effect is obvious; and it is clear also from equation (16) above that light-waves capable of disturbing an electron so as to enable it to escape would require to have a frequency in close agreement with the natural frequency of disturbed orbital motion of the electron.

We see, then, that the law of force (2), which we have been discussing, gives us an atomic system whose essential features are in conformity with Bohr's theory of the atom and with quantum theory. It admits also of equilibrium positions for an electron within the atom. The above discussion may be useful in providing a physical picture of an atomic system whose properties are similar in many respects to those of the Bohr atom, and in indicating a form of the law of force between an atom and an electron when atomic distances are reached.

CII. *An Oscillograph Study of the Aluminium Valve.* By F. H. NEWMAN, *D.Sc., A.R.C.S., Professor of Physics, University College of the South-West of England, Exeter**.

[Plate XI.]

1. *Introduction.*

WHEN diluted sulphuric acid is electrolysed with an anode of aluminium, the anode becomes coated with a grey film, and the polarization observed seems to be partly galvanic and partly dielectric. According to W. A. G. Schulze † the valve action of such an aluminium rectifier is due to the formation of a very thin layer of gas, of high resistance, and a thicker, porous layer of aluminium oxide, the pores of which are filled with electrolyte and gas. The whole may be compared with a condenser; since, however, the capacity and resistance of the formed anode are both very high, the charge accumulated cannot disappear in a moment. The resistance of the oxide layer appears to be very small in comparison with that of the gas layer, and the ohmic resistances are by no means constant.

F. Streintz and F. Fiala ‡, in experiments on gas generation from aluminium electrodes in diluted sulphuric acid, found that hardly any gas was liberated on open circuit; the electrolysis by 14 storage-cells gave very little oxygen at the anode, which collapsed in 24 hours. When the current was reversed before this collapse, the cathode—which had been the anode—gave the correct amount of hydrogen, and the relation between the current intensity in the anodic and cathodic directions, i_{12} and i_{21}, is

$$i_{12} = -\frac{a}{2} + \left[\left(\frac{a}{2}\right)^2 + bi_{21}\right]^{\frac{1}{2}},$$

where a and b are coefficients of practically equal value, and increase with the E.M.F. of the charging battery. The polarity

$$U = \frac{(i_{21} - i_{12})}{i_{21}}$$

increases with the charging potential V in such a way that UV becomes constant, starting from a certain value of V; that value of V is below 150 volts, but it cannot be fixed with any degree of accuracy. The value of U depends only upon the current density—increasing with the density—not upon V, provided that the density is not high. A valve effect was obtained by these experimenters only at high current density, and it depended upon the supply of anions per unit time.

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* Communicated by the Author.

† *Ann. d. Phys.* xxii. 3, p. 543 (1907).

‡ *Phys. Zeits.* xxii. p. 141 (1921).

Schulze[*] noted that during the formation of these electrolytic valves the P.D. rises first to the spark potential, then to the maximum potential, but sometimes there is a further slight rise. Both the porous film of the oxide and the effective oxygen film of high electrostatic capacity are exceedingly thin, especially the latter, and the film formation becomes more and more difficult as the temperature rises to 100° C. when more oxygen is liberated.

A. Smits[†] disagrees with Schulze's view that the passivity of aluminium during anodic polarization is due to the formation of a layer of alumina of high resistance. He considers that, although a coating of oxide or basic salt is formed at higher potentials, this explanation cannot be reconciled with the fact that at lower potentials, where passivity is also shown, the aluminium electrode remains bright, and that when the current is reversed the resistance disappears. Smits finds that, on anodic polarization, the potential of the metal becomes so strongly positive that the tension necessary for the separation of oxygen is reached with very low current densities. He considers that this change of potential is the primary phenomenon, and the separation of the oxygen, and subsequent oxide formation, is a secondary action. The increase of the aluminium potential is explained by the withdrawal of electrons from the metal being followed immediately by the aluminium going into solution. The formation of the aluminium ions within the solid metal proceeds with very slow velocity. Through the withdrawal of electrons and ions the metal surface passes into a state which resembles a metalloid, and it possesses an exceedingly small electrical conductivity. The aluminium surface, therefore, is a metal coating of great electrical resistance, and this coating is in turn surrounded by another of alumina.

The immediate destruction of anodic polarization on reversal of the current is explained by the fact that hydrogen, just as oxygen, though in a smaller degree, is a negative catalyst for the establishment of the internal metal equilibrium, but yet apparently acts positively catalytically when it separates on a metal surface that has previously absorbed oxygen, since both negative catalysts then disappear with the formation of water.

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[*] *Ann. d. Phys.* lxv. 3, p. 223 (1921).

[†] *K. Akad. Amsterdam,* Proc. xxii. 9 & 10, p. 876 (1920).

This valve action of aluminium has been utilized by the author * in a modified form of the Wehnelt interrupter, in which the cathode is an aluminium plate and a platinum wire acts as the anode, these electrodes being immersed in a saturated solution of ammonium phosphate. In addition to possessing rectifying properties, this arrangement also acts as an interrupter. The present work is an investigation of the valve action of this interrupter under various conditions.

2. *Experiments.*

In the experiments described below, the wave-form of the current passing the valve was investigated by means of oscillograms. The oscillograph employed was a Duddell permanent magnet type having a vibrator specially stretched so that, if necessary, it was able to follow variations in the current up to 1000 alternations per second. The resulting curves were photographed by means of a falling-plate camera. The plate release in the dark slide was controlled by an electromagnet, and the plate could be adjusted, if desired, at different heights, so that the time-interval between the commencement of the current and the instant of photographing could be varied and measured by using a special rotating commutator. The vibrator—in series with a high non-inductive resistance—was placed in shunt with the main current.

The valve consisted of an aluminium plate, 8 sq. cm. in area, and a platinum wire, 0·12 sq. cm. surface area, both electrodes being immersed in a solution of ammonium phosphate. Alternating current of period 60 was used, and, accordingly, the anode was formed by one-half of the current cycle, the other half tending to neutralize such formation. In all cases the P.D. is the maximum value, and the current density is expressed in virtual amperes as read from a hot-wire ammeter.

A clear surface of the aluminium having been prepared and placed in the electrolyte, the form of the current was observed and photographed at different time-intervals after the current had commenced to flow in the valve. The oscillograms Nos. I., II., and III. (Pl. XI.) represent the current form after such intervals of 0·2 sec., 0·6 sec., and 0·8 sec. respectively. Rectification, which depended on the current density, was complete with 1·05 amps. per sq. cm. within 0·8 sec., the strength of the anode film in this short interval being such that it withstands the applied P. D. of 100 volts. The time-interval required for complete rectification increases as the current density falls, but complete rectification is never attained with very small current densities, even when the applied voltage is as low as 12 volts. Oscillograms Nos. IV., V., and VI. give the current forms with current density 0·4, 0·2, and 0·11 amp. per sq. cm., and applied P.D. 50, 24, and 13 volts respectively.

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* Proc. Roy. Soc. A, xcix. p. 324 (1921).

Contrary to previous statements, it was found that the temperature of the electrolyte did not affect the rectifying properties of the valve. This is illustrated by oscillogram No. VIII., in which rectification is practically complete, although the valve was placed in an oil-bath and maintained at 96° C. The current density in this case was 0·96 amp. per sq. cm. and the P.D. —100 volts.

After anode formation, if the aluminium were removed from the solution and dried, the anode was not active on replacing it in the electrolyte, and in order to restore its rectifying properties it was necessary to remove the oxide film and re-form the anode. This fact seems to indicate that the thin gas film, which according to Schulze is present, is removed when the anode is dried.

Impurities present in the electrolyte have a detrimental effect on the rectifying properties of the valve, and sodium chloride appears to be very prejudicial in this respect. Oscillogram No. VII. shows the effect of adding a trace of this salt ; otherwise the conditions of the experiment were the same as those under which oscillogram No. VIII. was photographed. The chlorine ion appears to prevent the complete formation of the anode.

Self-induction in the circuit changes the form of the current curve and causes incomplete rectification. This is shown in oscillogram No. IX., in which the current density was 1·24 amps. per sq. cm., the P.D. 100 volts, and the self-inductance 20·5 henries.

The small time-interval necessary for the anode formation indicates that diffusion plays little or no part in the phenomenon. The film thickness must be very small, but, even so, the film is able to withstand a tension of 100 volts. A solid oxide film alone, without the existence of an oxygen layer, would be unlikely to maintain such a rectifying action. The fact that temperature has little effect on this valve action is important when the valve is used as an electrolytic interrupter. In the latter case considerable heat is developed ; and if the rectifying action ceased at high temperatures, this interrupter could not be employed with alternating currents, since in the event of such a cessation, the platinum wire, acting as the cathode during alternate half-cycles, would inevitably melt.

3. *Description of Plate.*

Oscillograms of A.C., period 60, rectified by the aluminium valve:—

I. Applied P.D. 100 volts. Current density 1·05 amps. per sq. cm. Current form, 0·2 sec. after current started.
II. Current form, 0·6 sec. after current started.
III. Current form, 0·8 sec. after current started.
IV. Applied P.D. 50 volts. Current density 0·4 amp. per sq. cm.
V. Applied P.D. 24 volts. Current density 0·2 amp. per sq. cm.
VI. Applied P.D. 13 volts. Current density 0·11 amp. per sq. cm.
VII. Effect of adding a trace of sodium chloride to the electrolyte. Other conditions the same as No. VIII.
VIII. Applied P.D. 100 volts. Current density 0·96 amp. per sq. cm. Temperature of electrolyte, 96° C.
IX. Applied P.D. 100 volts. Current density 1·24 amps. per sq. cm. Self-inductance in circuit 20·5 henries.

Except Nos. I., II., and III., the oscillograms were photographed 10 minutes after the current had been started, fresh aluminium being used in each experiment.

CIII. *The J Phenomenon in X-Rays.* (Part I.)

By C. G. Barkla, *F.R.S., University of Edinburgh**.

Introduction.

THE investigation of the J phenomenon has led to conclusions of such great interest and wide application that the writer is led to give a more complete and connected account of the subject than has been done hitherto. A number of short summaries and some fragmentary results have already been published †, but these reports have been very inadequate and cannot have conveyed any idea of the full significance of the experimental results. Though much work has been done and many facts have been learned, the study of the subject has only just begun to yield its most interesting conclusions. It is possible now to see in what direction we are moving, and to realize some of the consequences which necessarily follow, and others which will probably follow from the results of experimental investigation. A great deal of the work which has been done, might have been done much more accurately; we were however looking for large effects, and for results of fundamental importance rather than for accuracy in detail. These large effects we have found, and we now propose to give an account of them in as brief a form as possible. Brevity is indeed essential, for the subject has become too vast for a detailed account before the outlines have been indicated. Let it be said now that the J phenomenon has been observed between one and two hundred times, and without the least uncertainty. It is thus possible to give only a few examples of results obtained from the most interesting and significant experiments which have been undertaken. We should add that if some of these experiments were repeated other observations would be taken based on more complete knowledge of the phenomenon than was possessed at the time the experiments were made. It may, however, be a long time before we have opportunity to repeat all of these.

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* Communicated by the Author.

† Barkla, 'Bakerian Lecture, 1916,' Phil. Trans. 1917; Barkla & White, Phil. Mag. Oct 1917; Barkla & (Mrs.) Sale, Phil. Mag. April 1923; Barkla, 'Nature,' Nov. 17, 1923, and 'Nature,' Nov. 22, 1924; Barkla & Khastgir, Phil. Mag. Jan. 1925.

The results of experiments which are recorded will suggest many questions,—questions some of which can only be answered after further investigation. In some cases it will probably be wiser to withhold results until definite conclusions have been arrived at, rather than to excite speculation as to the probability of various possible alternatives. But though we are fully conscious of the vastness of the field which needs to be explored we have made definite tracks in many directions. In spite of the incompleteness of these investigations, a great deal of what appears to be of fundamental importance can be told. It is proposed to do this in several communications. A full and profitable discussion of the subject can only be undertaken when the experimental facts have been made known; this we shall proceed to do.

Early Investigations.

When making a study * of the relation between the energy of the K characteristic X-radiation emitted by an element and the number of electrons in the K corpuscular radiation associated with that particular characteristic radiation—a study which led to the conclusion that one quantum of K X-radiation was emitted subsequent to the ejection of each K electron—it was found that a sudden and quite unexpected increase occurred in the ionization in air when the X-rays reached a certain critical frequency, very much higher than the K frequencies for air. As such an increase of ionization had not previously been observed in any gas except in association with the emission by that gaseous substance of a characteristic X-radiation, this suggested the existence of a characteristic radiation of higher frequency than the K radiation—a J characteristic X-radiation.

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* See Bakerian Lecture, 1916.

Further investigation added to the evidence for the existence of such a characteristic radiation, for not only were all the usual accompaniments of the emission of a characteristic radiation observed from light elements, but a secondary radiation of more absorbable type than the primary was actually observed to be emitted; also it was observed only on the higher frequency side of what was approximately the same critical frequency.

Thus as a primary radiation of increasing frequency passed through a substance, while there was in general the usual diminution in absorption, at the critical penetrating power there occurred

(1) a sudden increase in the absorption of the primary X-radiation;
(2) a sudden increase in the ionization in the substance when that substance was in a gaseous state;
(3) an increase in the electronic emission from the substance when that was a solid in the form of a thin plate; and
(4) in the immediate neighbourhood of this critical frequency there appeared from the substance a secondary radiation more absorbable than the primary.

Previous to these experiments *any one* of these phenomena had been observed only in association with the emission of a characteristic radiation, of series K or L. The combination seemed overwhelming evidence for such a radiation, though the transformed radiation had not been shown to be characteristic solely of the element emitting it. It had been found to have features characteristic of the element, but had not been shown to possess a penetrating power characteristic *only* of the element. Especially was the evidence considered sufficiently convincing as the critical frequency varied from substance to substance, increasing with the atomic number of the element, as does the critical frequency associated with the K or the L radiations.

So much was recorded in the Bakerian Lecture for 1916

(Barkla, Phil. Trans. 1917). Since that time the reality of the phenomenon has been confirmed by scores of experiments, yet with all the similarities to the production of X-ray fluorescence, striking differences have appeared; and certain features have been brought to light which make the study of the greatest interest and importance.

It was hoped that long before the present time a more or less satisfactory explanation of the phenomenon might be found; but though much has been learnt and laws have been found, the phenomenon has been strangely elusive. The principal difficulties have arisen from two causes: firstly, the phenomenon is dependent on some factors which we have not yet been able to identify. It quite definitely occurs or does not occur, and we are left in no doubt as to which we are observing. But the feature distinguishing the experiments in which the above phenomena occur and those in which they do not occur, has not been recognized. As the J phenomenon occurs and does not occur under what appear to be identical essential conditions, it becomes exceedingly difficult to study the effect of a variation in conditions which are under control. Secondly, the phenomenon is so remarkable and has features so unlike anything with which we are familiar that nothing can be taken for granted. All the fundamental facts concerned with X-ray scattering and X-ray fluorescence as ordinarily known need to be investigated afresh in connexion with the new phenomenon. The phenomena of scattering and fluorescence, too, have their counterparts in optics, but the J phenomenon seems to open up quite new territory. The investigation is thus difficult for both practical and theoretical reasons; but much needs to be told, for it has an important bearing on many problems; indeed it appears to be intimately connected with that greatest problem of all—the problem of radiation itself. Though we cannot yet give the final solution, a knowledge of the phenomenon is essential if gross misinterpretations of experimental results are to be avoided. We do not propose to give a description of the apparatus used in all experiments—they are far too numerous. And it is not easy to see that much would be gained, for the apparatus and arrangement used in experiments showing the J phenomenon are identical with those in which the J phenomenon at other times did not occur. The results, however, cannot be described as irregularities, for one of the most remarkable features of the phenomenon has been its surprising regularity, when it does occur. The account given in this communication (Part I.) is little more than an introduction to the whole subject.

Absorption Experiments.

Absorption experiments were undertaken in 1915 and 1916 in order to determine if discontinuities occurred corresponding to those previously found in ionization when the ionizing radiations were characteristic radiations of the K series. They showed the discontinuity most markedly. In some of the earliest experiments, however, the radiation experimented upon was the radiation proceeding from an ordinary X-ray tube and filtered so as to eliminate the soft constituents. The pressure of the gas in the tube was varied and the thickness of filters altered so that the radiation used was the most penetrating portion of that emitted from the tube at different pressures. It was found by successive absorptions to be comparatively homogeneous. As the pressure of gas in the tube was reduced there was in general an increase in the penetrating power of the radiation emitted. The absorption in a given substance, however, exhibited a discontinuity, rising abruptly to a higher level and subsequently diminishing as previously with a diminution in the pressure of the gas in the tube. There was no doubt that the penetrating power and thus the frequency of the rays experimented upon varied steadily, for at the critical point in any substance the absorptions in all other substances progressively diminished as one would expect. But each substance showed its own discontinuity at a critical penetrating power depending upon the substance. Results obtained by Barkla and Miss White were published in the Philosophical Magazine in 1921.

The critical penetrating power was found to increase with the atomic number of the absorbing element.

It should be pointed out that in order to minimize any effects of heterogeneity in the beams experimented upon, a 50 per cent. absorption was always obtained when determining the absorption coefficients, and the absorption was calculated from the equation $I=I_0e^{-\mu x}$ as though the radiation was perfectly homogeneous. The magnitude of the sudden change in the value of $\frac{\mu}{\rho}$ was of the order of 15 per cent. There was not the slightest doubt of the reality of the phenomenon, for the step or discontinuity was quite large and could be traversed repeatedly in either direction; it could not escape observation. Such a step was, of course, quite familiar since the discovery by Barkla and Sadler of the K absorption edge associated with the K characteristic radiation.

Unusual features only very gradually began to appear.

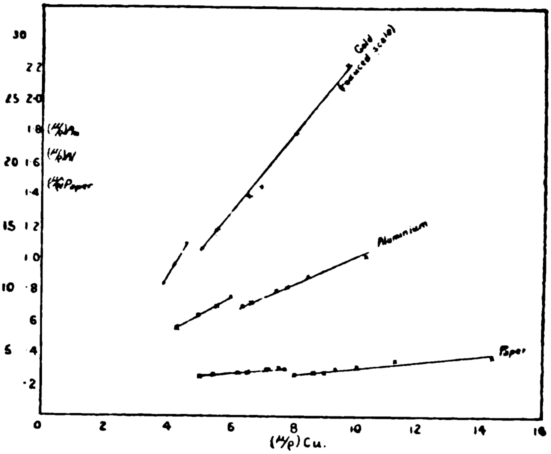
The first noteworthy point was the abruptness of the change in absorption. Other experiments did, it is true, indicate that the radiations used were unusually homogeneous, but from our experience of the K and L absorption discontinuities, we did not expect the change to be quite so sudden. When a heterogeneous beam is gradually hardened up, though the absorption of a homogeneous constituent may be regarded as rising suddenly as it passes the K or L critical absorption frequency, owing to heterogeneity the total absorption rise is gradual; but the J discontinuity was found to be absolutely abrupt even when a very heterogeneous radiation was used. This effect is as though the whole absorbing property of the substance was suddenly increased for every constituent of the complex radiation, and then subsequently the absorption changed in the normal way with increasing frequency, but at the higher absorption level.

In many of the following experiments no attempt was therefore made to produce even approximately homogeneous beams, for these heterogeneous radiations provided us with the phenomenon which we wished to examine. In one set of experiments, for example, the heterogeneous X-radiation scattered from very thick plates of aluminium was used. As the primary beams exciting this radiation varied in penetrating power, the absorption of the scattered radiation was measured in several substances. The discontinuities again appeared exactly as they had done in experiments on primary radiations. The results obtained for the absorption by paper, aluminium, and gold on three consecutive days are shown in fig. 1. This figure should be compared with that published by Barkla and Miss White obtained from their experiments on filtered primary beams direct from an X-ray tube. The agreement in position and magnitude of the discontinuity is remarkably close.

Using such scattered radiations, the discontinuities occurred without interruption for a long period, and we concluded that the scattered radiation was much more susceptible to the phenomenon than was the primary radiation. The two, of course, differed in these respects,—the primary beam necessarily consisted of a few narrow pencils; the scattered radiation was a wide beam: the primary was practically unpolarized; the scattered radiation highly polarized: the primary was comparatively intense; the scattered radiation was feeble.

Later experiments, however, showed that even the scattered radiation did not always exhibit the phenomenon; the discontinuity disappeared and was not observed for a long period. Thus at times the perfectly regular linear relationship between the absorptions in various substances was obtained; at others, though the experimental conditions were apparently identical, the J absorption discontinuities were obtained without the least uncertainty, and at the penetrating powers characteristic of those substances. It thus appeared that there were two possible absorptions in a given substance, some apparently slight change in the conditions of the radiation deciding which absorption would occur.

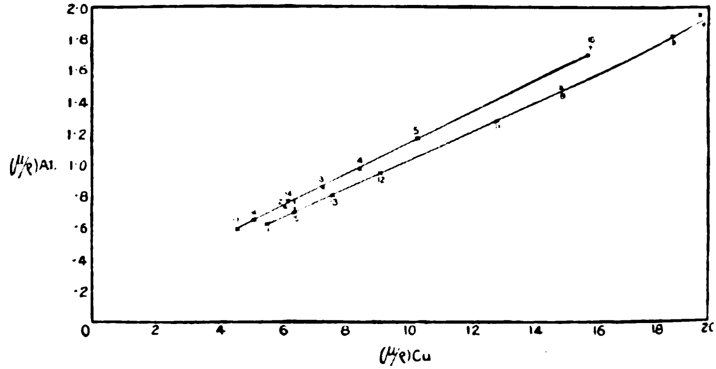
Fig. 1.



It is of course evident that if the controlling factor varied during a series of observations, the discontinuity might occur at any penetrating power within the range of penetrating powers over which there are two possible absorptions. This very rarely happened, however, for above the critical penetrating power the absorptions in a given substance were almost invariably at either the lower or the upper absorption levels, not fluctuating from one to the other, during a series of observations.

Perhaps the most striking exception to this rule which we venture to give is shown in fig. 2, in which absorptions in aluminium are plotted against absorptions in copper. The numbers indicated by the various observational points indicate the order in which the observations were made. They show that though all the points lie fairly accurately on two straight lines, there are in a series of 17 observations as many as 9 changes from one level to the other. The radiation was evidently somewhere about the state of instability between the two different states; it was very sensitive to the unknown controlling factor. This experiment (though it is such an outstanding exception among this particular series) does show that the higher absorbing level may be reached by radiations of frequency considerably lower than the J critical absorption frequency. This conclusion receives ample support from experiments on the scattering of X-rays to be described in later papers. It should be noticed that in the latest observations from 11 onwards, *i. e.* when conditions had apparently settled down, there was the usual sudden rise in the absorption in aluminium at $\frac{\mu}{\rho} = \cdot 7$ approximately*.

Fig. 2.



A remarkable feature then is the fact that the absorption discontinuity occurred so persistently at the same critical penetrating power for a given substance. This may be seen, for instance, from the various figures in this paper, though they are selected to illustrate different points. The discontinuity in aluminium is at a value of $\frac{\mu}{\rho}$ in Al of 0·7,—this being calculated from a 50 per cent. absorption. This has been observed more than 30 times, that is in over 30 distinct experiments, in many of which the step was traversed several times in both directions.

As previously stated, the position of the absorption step depends upon the atomic number of the absorbing element, an increase in the atomic number being accompanied by a displacement of the absorption step towards the more penetrating end of the spectrum; that is, by an increase in the critical absorption frequency—a result agreeing with that originally obtained by Barkla & Sadler for the K absorption edges. The J discontinuity did not, however, occur nearly so frequently in copper as in aluminium—the only two substances upon which the numbers of experiments were comparable,—consequently in plotting the results the absorption in copper was usually taken as the standard.

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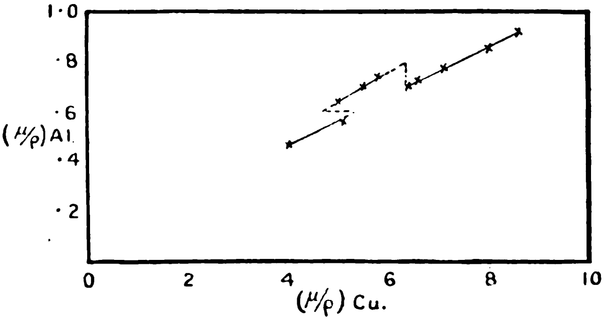
* See observational points, 11, 12, 13, 14, 15, 16, and 17 in fig. 2.

Fig. 3 shows the result of one experiment in which both aluminium and copper showed the discontinuity,—when the relative absorptions returned to the original line approximately. (Without other evidence it might be thought that the absorption in aluminium returned to the lower level again: the absorption in aluminium, however, varied progressively with the gas pressure in the X-ray tube throughout the copper discontinuity.)

Fig. 3.

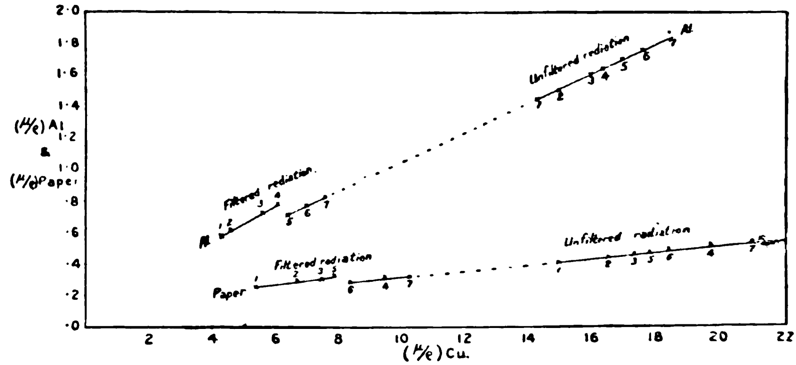


Such discontinuities have been found in all substances tested, *i. e.* by the absorption method in carbon (in paraffin wax), oxygen (in water and in paper), aluminium, copper, platinum, and gold; and by other methods in nitrogen, sulphur, and lead.

Another remarkable feature of the phenomenon is that with beams obtained in so many different ways the critical penetrating power should appear so constant. In fact, the discontinuity appears to depend more closely upon the absorption coefficient of the radiation than upon mere wave-length. This is illustrated very distinctly in several ways.

Thus a heterogeneous beam direct from an X-ray tube when gradually made more penetrating may exhibit no absorption discontinuity, whereas the same beam when filtered and so brought to a higher average penetrating power shows the discontinuity quite clearly and at the correct critical point. Thus fig. 4 shows two absorption curves, the upper one for aluminium, the other for paper. The upper curve shows in its right branch the relation between absorption in aluminium and absorption in copper for a beam direct from an X-ray tube. The left branch, which it will be observed is broken into two sections, shows the relationship between the two same quantities when the primary beam had been filtered by ·0058 cm. of copper; the filtered beams of course were of much higher average penetrating power than the unintercepted beams. The results of absorption experiments on the same beams unintercepted and filtered are indicated by the same number

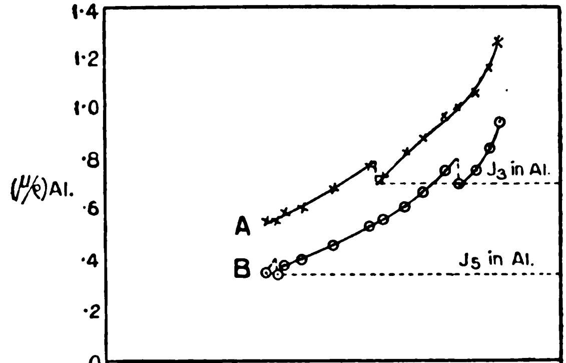
Fig. 4.



on the figure; thus (1) on the curve for the filtered portion corresponds to (1) on the curve for the unintercepted. As the tube was hardened progressively from 7 to 1 there was a progressive fall in the absorption of the unintercepted beam by aluminium, but the filtered beam exhibited a sudden increase in the absorption from the state 5 to the state 4 (see figure). According to all accepted ideas every constituent in the filtered beam was also in the unintercepted beam, yet the absorption step was not indicated to the slightest extent in the unintercepted beam. It should be noticed that the discontinuity occurred at the same point—*i. e.* the same value of the absorption coefficient in aluminium $\left(\frac{\mu}{\rho}=\cdot 7\right)$—as in the results shown in fig. 1 for the scattered and otherwise unfiltered beams. The lower curve in fig. 4 shows the corresponding phenomenon in paper. In this case again the discontinuity appeared in the absorption (by paper) of the filtered beam and not of the unintercepted beam; but it occurred at the absorption coefficient characteristic of paper and agreeing with the results of experiments obtained by Barkla & White with primary beams and those already recorded in this paper and made upon scattered beams.

Again, two beams proceeding from the same tube at the same time in different directions may have different penetrating powers. (We did not investigate the cause of this; there were various possibilities. These did not appear of any special interest at the time, though now we find there is strong evidence that the difference is itself associated with the J phenomenon; it is like the difference between a primary and a scattered radiation as frequently observed.) As the tube hardens up, the absorption step or discontinuity occurs in each beam when that particular beam reaches the critical penetrating power, and not when the tube reaches a certain state or begins to emit certain rays. This is illustrated in fig. 5, in which the two curves A and B show by their

Fig. 5.



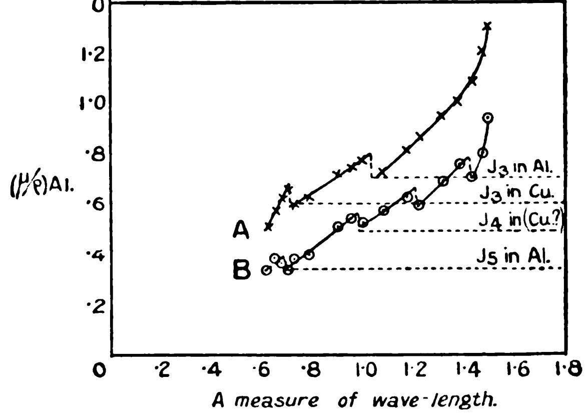


Fig. 6.

ordinates the absorption coefficient in aluminium of the two beams from the same tube. The abscissæ give a rough measure of the effective wave-length of radiation proceeding from the tube. (It is unnecessary to indicate the method of measurement; it was based on the path of the electrons ejected by this radiation) Beginning at the right-hand side both curves show the progressive diminution in the absorption by aluminium as the effective wave-length is diminished, except at the critical point $\frac{\mu}{\rho}$ in aluminium $= \cdot 7$ (and much less clearly though perhaps not less markedly at the value of $\frac{\mu}{\rho} = \cdot 33$ approximately). Each beam, when its absorbability reached the critical value represented by $\left(\frac{\mu}{\rho}\right)_{\mathrm{Al}} = \cdot 7$, showed a marked increase in the absorbability. For the softer radiation (the upper curve) the tube was in a harder state than for the other before it showed the absorption rise,—that is, the rise in absorption appeared not for a given state of the tube, but when a given penetrating power was reached. It should be stated that the beams had both been filtered by a constant thickness of about ·5 cm. of aluminium.

Fig. 6 shows the results obtained immediately afterwards under similar conditions except that the radiations were filtered by ·0141 cm. of copper instead of ·5 cm. of aluminium before being absorbed by aluminium. The features of fig. 5 appeared again, and in addition another discontinuity in both curves,—in this case the discontinuity in copper, for it occurred at precisely the penetrating power found for copper in other experiments. Thus as a radiation of increasing frequency from an X-ray tube was transmitted through copper, at the critical point for copper there occurred an increase in the absorbability in a second substance (aluminium).

Thus the radiation which exhibited the characteristic increase in absorption in copper was after transmission through copper more absorbable to aluminium also. This was additional to the change which took place in aluminium itself. The radiation was thus by its passage through copper truly transformed; its properties were changed in such a way as to make it more absorbable in some substances at least.

Fig. 7 was obtained in a similar way to fig. 5 and a few days subsequently. The discontinuities had entirely disappeared.

Further, in some cases, the discontinuity is not observed when thin sheets, absorbing only a small fraction of a beam, are used to measure the absorption coefficient, whereas thick absorbing sheets exhibit the discontinuity. This is illustrated in fig. 8, in which the lower graph shows the values obtained by using the thickness of absorbing material which cut off

Fig. 7.

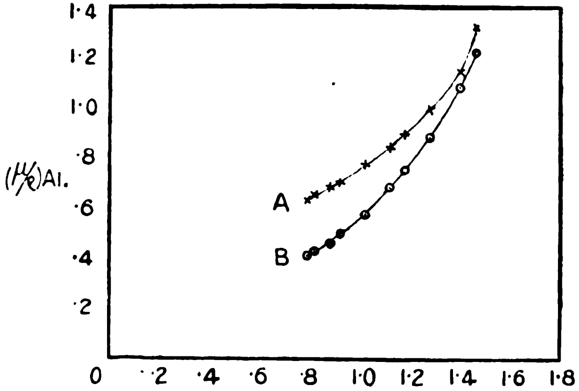
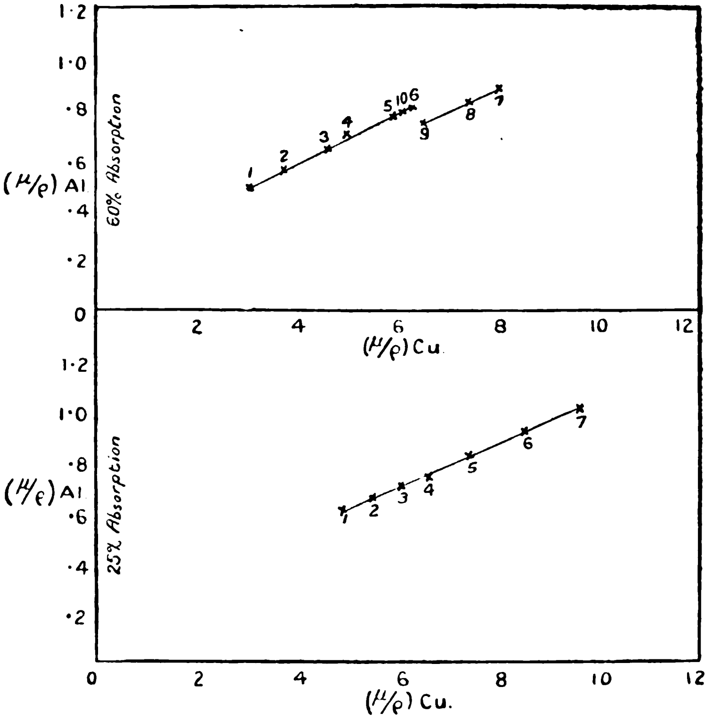


Fig. 8.



only 25 per cent. of the radiation, or more precisely 25 per cent. of the ionization produced by the radiation, while the upper graph was obtained from measurements in which as much as 60 per cent. was absorbed. The rise to the higher level of absorption in aluminium appeared only in the 60 per cent. absorption graph. The straight line on the graph for 25 per cent. absorptions is precisely a continuation of the lower branch obtained in the 60 per cent. absorption. It is evident then that the discontinuity must occur at some critical thickness of the absorbing sheets.

Fig. 9.

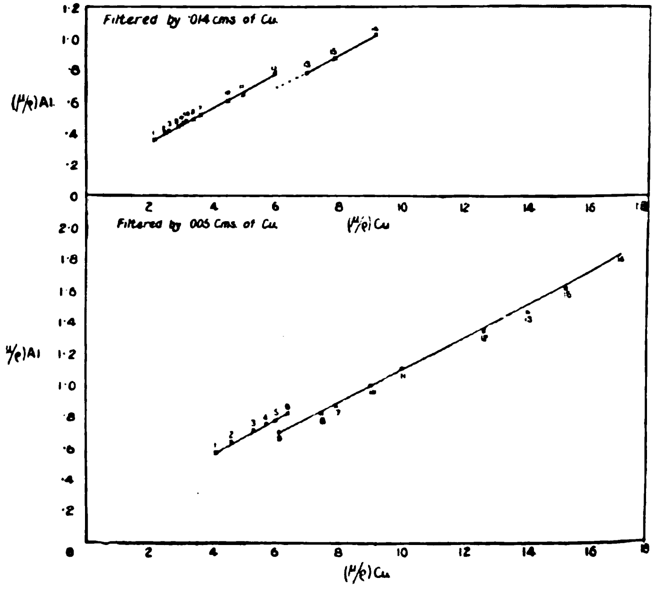
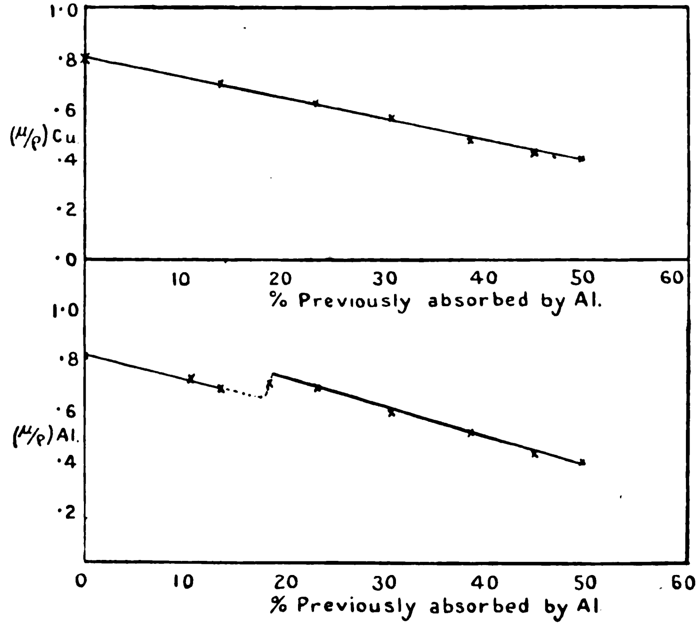


Fig. 9 shows the relation between absorption in aluminium and absorption in copper for the same radiation filtered by two different thicknesses of copper. In this case, however, the thickness of the absorbing sheet (by which the 'absorption coefficient' was determined) was the same in both cases. The lower graph gives the relation for the beam transmitted through ·005 cm. of copper, and the upper graph for the same radiations transmitted through ·014 cm. Corresponding numbers on the two graphs indicate radiations which were identical before transmission through these differing thicknesses of copper. Commencing at the low frequency end and gradually increasing the frequency, *i. e.* moving from right to left of the figure, the discontinuity appeared very early for the beam transmitted through thick copper, and much later for the beam transmitted through the thin sheets. But in both cases it occurred when the average value of $\frac{\mu}{\rho}$ in aluminium reached the value 0·7. Again, according to present ideas, this is a strange result, for the radiations at which the discontinuities occurred were presumably of quite different character; what was common was a certain rate of absorption as measured by ionization methods. The two curves superpose perfectly, giving the one discontinuity.

Fig. 10.



Such results led to an examination of the effects of successive thin filtering sheets on a heterogeneous radiation. The average absorption coefficient calculated from the relation $I = I_0 e^{-\mu x}$ (as though the radiation were homogeneous) was determined after the radiation had been transmitted through increasing thicknesses of aluminium. Thus in fig. 10 the value of $\frac{\mu}{\rho}$ in aluminium and $\frac{\mu}{\rho}$ in copper (calculated as indicated) are plotted against the amount of radiation previously absorbed by aluminium—as measured simply by diminution of ionization produced by the beam in an ionization chamber. In one case the discontinuity is shown by the rise in the absorption in aluminium, while in the other case the absorption in copper even after transmission through the same thickness of filtering aluminium shows no sudden increase. This indicates that the discontinuity occurred not in the process of filtering but in the final absorbing sheets by which the absorbability was tested. The filtering sheets were, however, essential to the discontinuity found in the absorbing sheets. (At the time of the experiment we did not realize that the discontinuity would not have occurred at the critical point indicated except for the last thin layer of the absorbing sheet.)

Fig. 11.

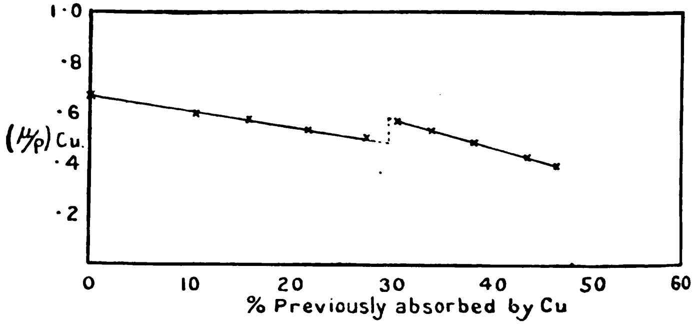


Fig. 11 shows a corresponding discontinuity in the absorption in copper when the primary beam was filtered by copper. Again, this appeared at the critical absorption coefficient characteristic of copper,

Thus as a heterogeneous primary beam is increased in penetrating power as a whole, or even has its average penetrating power increased by the process of filtering, there occurs an abrupt increase in the absorbability of the radiation in a particular substance. The critical penetrating power at which the discontinuity occurs is characteristic of the absorbing element. The transmitted beam is, however, subsequently more absorbable in other substances also. The critical penetrating power varies only very slowly with the atomic number of the absorbing element, but it is in the same direction as for the K, L, or M absorption edges.

The following values have been obtained for the position of the J absorption steps in C, O, Al, Cu, Pt, Au, these being expressed as mass absorption coefficients in Al, and in approximate wave-lengths :—

J_3 Absorption Steps.

Approximate Absorption Coefficients $\left(\frac{\mu}{\rho}\right)_{Al}$

	C.	O.	Al.	Cu.	Pt.	Au.
Barkla & White	1·05	0·84	·7	$<$·6$>$·54	—	—
Barkla & Stevens ...	—	·82	·7	·6	·57*	·54*

Approximate Wave-lengths †—Ångström Units.

C.	O.	Al.	Cu.	Pt.	Au.
·39	·355	·335	·315	·305	·30

* Reduced to the lower level.

† Converted to wave-lengths from S. J. M. Allen's table (Phys. Rev. July 1924).

Though these discontinuities have been obtained in this laboratory by several experimenters the agreement between the values is remarkably close.

All the radiations experimented upon were the primary rays from an X-ray tube, filtered by aluminium or copper in order to eliminate the softer constituents ; or they were X-rays scattered from thick sheets of light substances. These discontinuities were first studied with the help of Dr. Margaret White ; some of the results were recorded in a paper by Barkla & White (Phil. Mag. Oct. 1917). It was afterwards observed that the discontinuites had appeared in the results of earlier experiments, but as the results were used for other purposes the discontinuities had passed unnoticed. All the results exhibited in this paper were obtained with Mr. Stevens. The discontinuities of this particular series J_3 have been observed between 70 and 80 times under various conditions ‡.

The much more homogeneous rays constituting the characteristic radiations of the K series have also been experimented upon, and similar discontinuities have been found in the absorption of these—as recorded in the Bakerian

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‡ The J_3 absorption step in aluminium was obtained by the spectrometer by Dauvillier (*Annales de Physique*, vol. xiii., 1920) for a wave-length ·358 Å.U. The agreement is probably as close as the accuracy of the relation between absorption-coefficient and wave-length will permit.

Lecture for 1916 (Phil. Trans. 1917). Initially there appeared to be a discrepancy between the values of the critical mass-absorption-coefficient obtained for these characteristic rays and those given above under the heading J_2 and obtained from experiments on more heterogeneous primary rays. It was seen, however, that the difference between the critical values of $\left(\frac{\mu}{\rho}\right)_{Al}$ for the primary radiation and for the fluorescent characteristic radiation was quite a consistent one. In fact, the positions of the absorption steps obtained by using characteristic radiations seemed to be just those obtained by primary rays shifted along towards the longer wave-length end of the spectrum by 20 per cent. to 25 per cent. increase of wave-length. It originally appeared probable that this discrepancy was due to the difference in the constitution of the two beams—one a primary, giving presumably a continuous spectrum within narrow limits, and the other the characteristic radiation giving a line spectrum approximately consisting of radiations of two neighbouring wave-lengths. Fortunately, however, such a complication does not appear to express the truth, for we have found that these two form quite distinct series and may *both* be obtained in experiments upon certain radiations (Barkla & Khastgir: unpublished).

The only values in this series obtained from direct absorption experiments upon characteristic radiations are those for oxygen and aluminium. Sulphur and copper discontinuities have also been obtained using characteristic radiations, but they have been by ionization methods—methods indeed which are much more sensitive than the absorption method. But of these more later. The values obtained with Dr. Khastgir on heterogeneous scattered X-rays are also given under the heading J_2. Thus the J_2 discontinuities were first observed in work with Mr. Hagger; these were ionization discontinuities. The J_2 absorption discontinuities and the corpuscular emission discontinuities were searched for and found with Dr. Margaret White. These were all in experiments on characteristic radiations of the K series. They have since been observed in experiments with Dr. Khastgir on the absorption of more heterogeneous scattered radiations, and apparently by E. A. Owen and by C. M. Williams, using the more homogeneous radiations obtained by the spectrometer (Proc. Roy. Soc. A, xciv., 1917).

The various values obtained are given below :—

J_2 Absorption Steps.

Approximate Absorption Coefficients $\left(\frac{\mu}{\rho}\right)_{Al}$

	N.	O.	Al.	Si.	S.	Cu.
Barkla, White, & Hagger	2·5	2·5 to 2·2	1·8	—	1·7	—
Barkla & Khastgir...	—	2	1·8	—	—	(2·3?)
C. M. Williams	—	—	2	—	—	1·46*
E. A. Owen	—	—	—	1·85*	—	—

Approximate Wave-lengths—Ångström Units.

	N.	O.	Al.	Si.	S.	Cu.
	·55	·5	·49	·493	·48	·45

* Obtained from wave-lengths given in papers by E. A. Owen and by Williams.

Again, a further series of absorption discontinuities has been found in experiments with Dr. Khastgir upon the secondary X-rays scattered from light substances. These are in the region of more absorbable radiations—lower frequencies. These are indicated below :—

J_1 Absorption Steps.

Approximate Absorption Coefficient $\left(\frac{\mu}{\rho}\right)_{Al}$

O.	Al.	S.
>4	3·8	3·5

Approximate Wave-lengths—Ångström Units.

O.	Al.	S.
>·66	·63	·61

Also in addition to the above we have previously recorded similar absorption discontinuities for the elements carbon and oxygen at a value of $\left(\frac{\mu}{\rho}\right)_{Cu}$ of about 3·5 corresponding to a value of $\left(\frac{\mu}{\rho}\right)_{Al}$ equal to about 0·47 or to a wave-length of 0·28 Ångström units. There appears to be little doubt then of a similar series of discontinuities in this region. This J_4 series is what Barkla & White referred to as a possible I series when it appeared that only one J series was known.

And finally, quite independent discontinuities have been observed in aluminium at a value of $\left(\frac{\mu}{\rho}\right)_{Al} = {\cdot}34$ or a wave-length of approximately ·23 Å.U.† These are shown in figs. 5 & 6 and appear in other experimental results.

† Dauvillier gave evidence for a value ·228 Å.U. in Bromine.

Thus there have been observed what appear to be three distinct series of these J absorption discontinuities, and what are probably isolated results in two further series. We have been in the habit of distinguishing between them by describing them as the first or second and so on, and for the present we shall name them the J_1, J_2, J_3, J_4, J_5 steps, J_1 being among moderately soft radiations (say about ·6 Å.U.) ; the J_2 among the slightly more penetrating radiations and in the neighbourhood of ·5 Å.U.; J_3 the series given by Barkla and White and in the neighbourhood of ·3 to ·4 Å.U.; and others in the region of high frequencies and between ·2 and ·3 Å.U.

No high degree of accuracy is claimed for these values of critical absorption coefficients or their equivalents in wavelengths. When a heterogeneous radiation is being experimented upon, it is probably the value of $-\frac{1}{I\rho}\frac{dI}{dx}$ just before the discontinuity occurs that should be determined. But our method gives a result which usually differs little from this. And of course when the discontinuity occurs, absorption coefficient as calculated ceases to have any precise meaning. Further, even away from a discontinuity the absorption coefficient does not define the radiation—it is not unique. But these are all points for a later paper, when the broader facts have been outlined.

Critical Conditions.

Attempts to discover the difference between the conditions of experiments which showed, and those which did not show the J phenomenon, have so far been unsuccessful.

The J phenomenon occurs sometimes and at other times does not occur with strong, and with very feeble radiations ; with highly polarized, and with unpolarized radiations ; with narrow pencils of radiation such as would produce an ionization almost entirely outside the radiation, and with wide beams producing the bulk of its ions within that beam ; with heterogeneous radiations, and with approximately homogeneous radiations ; with radiations from many different tubes, and with different anticathodes ; with primary radiations, scattered radiations, and characteristic radiations. Various methods of measuring the intensity of the Röntgen radiation have been adopted. Ionization in air, in sulphur dioxide, and in hydrogen, produced by the emission of high-speed electrons from an aluminium plate in the path of the X-rays, and ionization produced by high-speed electrons ejected from copper, have all been used to measure the intensity.

The discontinuity has been observed by each of these methods and at the same critical penetrating power. It should be noted, however, that all such methods of measuring an X-radiation are based on what is admittedly an action of X-rays governed by quantum laws. All directly observable actions are probably governed by such laws. We must therefore for the present regard all such measurements as measurements of the X-rays themselves. We shall, however, have more to say of this in later papers.

We have observed the effect with a dozen or more arrangements of apparatus. Though we have frequently looked for effects produced by a change of X-ray tube or by its method of excitation, by changes of absorbing material—replacing absorbing sheets after prolonged exposure to X-rays by quite fresh and previously unexposed sheets,—we have never observed any evidence of dependence on these things. Sometimes the J discontinuity occurred day after day; at other times it could not be observed for a comparable period. More remarkably still, at certain times the J effect appeared and disappeared before our eyes, while we were unable to detect any change in the conditions. Further experiments on this point will be described later.

Thus though heterogeneity or feebleness or polarization may be favourable to the phenomenon, not one of these factors is essential. Neither can the critical factor be essentially in the absorbing substance, for reasons given above.

The critical condition appears then to be provided either by the X-radiation or by something with the X-radiation or by some external influence superposed upon the radiation.

Comparison with other Absorption Discontinuities.

It will have been observed that this J absorption phenomenon, though superficially so like the K absorption phenomenon associated with the emission of K characteristic radiation, has many unique characteristics which are of the greatest importance theoretically. There are, indeed, many features which distinguish it from anything previously known. The most striking are the following:—

1. The phenomenon is conditional on some factor or factors which have never previously been considered as a governing factor in X-ray phenomena. The only condition essential to X-ray fluorescence and the accompanying K, L, or M absorption phenomenon is (as far as has been discovered) that the radiation should possess some constituent of frequency

greater than the critical absorption frequency (Stokes' law)*.

2. The sudden changes in absorption occur with surprising abruptness; indeed there appears to be an absolute discontinuity as though every constituent of the radiation being absorbed were suddenly absorbed at a higher level. In fact, the discontinuity in absorption appears to be quite as perfect when a heterogeneous beam is used as when the most homogeneous radiation is employed. Thus if the constituents were independent, the rise in absorption would be very gradual, occurring for each constituent as it passed the critical absorption frequency.

3. The discontinuity is much more closely associated with an absorption coefficient than with a certain wave-length.

According to all present conceptions, the filtered radiation contains the same constituents as the unfiltered though in different proportions, yet frequently only the filtered radiation shows the discontinuity. Change in intensity (alone and of the magnitude produced by filtering) has not been found to produce the result; it is due to a change in the properties of the radiation produced by transmission through matter.

4. When the rise of absorption has occurred in a substance, the transmitted radiation is found to be more absorbable in other substances quite independently of the fact that these other substances exhibit their own absorption discontinuity (increased absorption). Thus the transmitted radiation is a transformed radiation as far as its penetrating power is concerned.

5. The change of critical absorption coefficient with atomic number of the absorbing substance is very small and diminishes with increasing atomic number.

6. The series of critical absorption coefficients in the various elements cuts right across the well-known K series.

Summary.

The paper gives a brief general account of the J absorption discontinuities with a few illustrations of the results obtained. They show that as the penetrating power of a radiation is increased either (1) by increasing the speed of the electrons which excite it, (2) by selection of the characteristic radiations from elements of increasing atomic number, or (3) even by the process of filtering a heterogeneous radiation, there occur sudden increases in the absorption of the radiation by any particular substance.

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* First stated by the writer for X-rays in 1909, Proc. Phil. Soc. Camb.

In the first two cases this is very similar to the rise in the absorption in a substance accompanying the emission by that substance of a characteristic radiation ; but the production of the effect by mere filtering is a result of quite a new kind. It will be discussed when other results have been described. This absorption discontinuity occurs at higher frequencies (higher penetrating powers), the higher the atomic number of the absorbing element.

Absorption discontinuities have been observed directly in carbon, oxygen, aluminium, copper, platinum, and gold ; and indirectly—by the accompanying ionization—in nitrogen, sulphur, and lead. They all fall into several series, J_1, J_2, J_3, and there are isolated cases indicating further probable series, J_4 and J_5.

It has already been shown, and will be further shown in a later paper, that the increase in absorption is accompanied by the emission of slowly moving electrons from the absorbing substance, producing, when that substance is in a gaseous state, an even more strongly marked discontinuity in ionization.

Features distinguishing the sudden rise in absorption from that accompanying the emission of a K or an L characteristic radiation are given.

Some of the most remarkable conclusions from the experiments are the following :—

There are alternative absorptions possible for what are *to all appearance*—*i. e.* from close examination by other methods—identical radiations. Corresponding to these alternative absorptions there are alternative corpuscular emissions and alternative ionizations in the substances exposed to the X-rays. Indeed the actions of X-rays (which means the quantum actions, for the actions referred to are governed by the quantum laws) depend upon factors other than wave-length of a radiation and the atomic number of the substance traversed. In other words, the activity of an X-ray radiation is dependent on factors which have hitherto not been taken into consideration.

(This paper definitely shows only two levels of activity; it indicates the existence of several, the complete evidence for which will be given later.)

Thus the emission of electrons—the photoelectric effect of X-rays—for rays of a given wave-length is not proportional to intensity ; other factors are operative. In fact, experiments seem to show that as far as the J phenomenon is concerned the penetrating power of a complex radiation is a more fundamental quantity than the wave-length or the wave-lengths of its constituents. The phenomenon appears to suggest the separation of the quantum actions of radiation from the frequency of radiation.

The results of more detailed investigation and a more critical discussion will follow.

In conclusion I wish to express my great indebtedness to Mr. W. H. Stevens for his invaluable assistance in all the experimental work, the results of which are recorded in this paper.

[To be continued.]

CIV. *On Eddington's Natural Unit of the Field.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I REGRET that in a paper contributed to your Journal [No. 290 (Feb.), pp. 457–463] I made a serious blunder, to which Dr. Silberstein has kindly called my attention in a private communication. On page 461 I state that recent investigation has increased the estimated value of R, the world curvature-radius, from the order 10^7 parsecs to a much higher order, and in particular refer to an estimate of Dr. Silberstein's of the order 10^{12} *parsecs*. Actually the values derived by him are of the order 10^{12} *astronomical units* (6×10^{12} astr. units by one method, $7{\cdot}2 \times 10^{12}$ by another). The order of magnitude for R is thus much the same as before, and this mistake on my part completely destroys any numerical support for my equation (7) and renders the particular speculation on page 462 quite valueless.

May I, however, point out that Dr. Silberstein's value of $7{\cdot}2 \times 10^{12}$ astr. units for R produces a remarkable numerical coincidence with regard to another speculation concerning "*h*." On page 380 of my book on 'Relativity' I have drawn attention to the fact that if one multiplies the energy-density of Eddington's unit-field by the volume of the electron and, taking this as a unit of energy, multiplies it by the "cosmic" unit of time R/c, the result is a unit of action of the order 10^{-27} if R is assumed to be of the order 10^7 parsecs. Owing to my foolish mistake concerning Dr. Silberstein's value of R, I believed that all numerical support for such an idea had gone (and was thus led to the suggestion made in the paper); whereas I find that, on the contrary, the actual value fits the speculation quite well. In fact, if one takes the unit of action calculated in the manner above to be equal to h, it is easy to derive the equation

$$\frac{r^2}{R\rho}=6\frac{hc}{e^2},$$

which replaces equation (7) of my paper. Now, the right-hand side is 6 × 861 or 5,166; and if we adopt these values,

$$r=1{\cdot}88\times10^{-13},$$

$$\rho=\kappa m=7{\cdot}4\times10^{-29}\times9\times10^{-28}=6{\cdot}66\times10^{-56}\text{ cm.},$$

$$R=7{\cdot}2\times10^{12}\text{ astr. units}=1{\cdot}06\times10^{26}\text{ cm.},$$

the left-hand side works out practically 5,000.

I ought to state also that the order of magnitude of the unit-field is an electrostatic unit, not the much smaller value mentioned in the paper.

Yours faithfully,
J. Rice.

George Holt Physics Laboratory,
The University of Liverpool.
March 25, 1925.

CV. *Low-voltage Arcs in Sodium and Potassium Vapours.* *By* F. H. Newman, *D.Sc., A.R.C.S., Professor of Physics, University College of the South-West of England, Exeter*[*].

1. *Introduction.*

It is now a well-known fact that arcs may be established in most vapours bombarded by electrons, the energy of these electrons being considerably less than that which would be expected on the quantum theory. In some cases the required voltage between the electrodes is only slightly greater than the resonance potential of the vapour, a correction factor being applied for the initial kinetic energy of the electrons emitted from the incandescent filament cathode. R. W. Wood and S. Okano[†], who carried out an extensive series of experiments with sodium vapour, concluded that the D lines appeared when the potential between the hot cathode and the anode was as low as 0·5 volt, and various experiments showed that the emission of the D lines, under these circumstances, could not be ascribed to any secondary action, such as the light from the incandescent filament. Such a result would appear to be in conflict with the quantum theory—namely, that the ionization potential is given by $V=\frac{(1s)h}{e}$ where 1*s* is the frequency of the shortest wave-length in the principal series $\nu=1s-mp$; but there are at least three factors which must be taken into account in explaining the striking and maintenance of arcs below the ionization potential.

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[*] Communicated by the Author.

[†] Phil. Mag. xxxiv. p. 177 (1917).

The valency electron, within the atom, may be ejected from the normal orbit to the adjacent outer orbit by an inelastic collision with a bombarding electron, and, while the atom is in this excited or abnormal condition, a second collision with another bombarding electron may occur which results in the complete ejection of the valency electron from the atom. In the case of sodium, for example, the atom may be bombarded by an electron of energy corresponding to 2·12 volts—the resonance potential of sodium vapour—and while it is in the excited state, collision with another electron raises the valency electron to a higher energy level, or outer orbit, ultimately producing ionization. It is evident that the probability of ionization by successive impacts in this manner depends upon the average time-interval within which the excited atoms remain in the abnormal state. From Stark's work * on helium this time-interval appears to be 10^{-8} sec. approximately.

Another controlling factor in the operation of low-voltage arcs is the phenomenon of the absorption of radiation which is emitted when the atoms resume their normal conditions. The valency electron, in a sodium atom, returning to the 1*s* orbit from the 2*p* orbit will give rise to the D-line radiation, which may be absorbed by any neighbouring sodium atom, resulting in the ejection of the valency electron in this latter atom to the 2*p* orbit. The excited atom, thus formed, may then collide with another bombarding electron which completely ionizes the atom. The radiation $1s-2p$, emitted in the first instance, may be diffused throughout the vapour in all directions and, as K. T. Compton † has shown, this ionization, by what he terms "photo-impact," is relatively of far greater importance, especially at high vapour pressures, than ionization by successive impacts. Ionization by "photo-impact" may be the result of several such radiation absorptions followed by a single electron impact of energy corresponding to the resonance potential, so that in this case it would be possible to produce complete ionization of the vapour with electrons none of which have a velocity greater than that corresponding to the resonance potential. In actual practice the striking voltage of the arc should be equal to the difference between the minimum ionizing and resonance potentials, less the average emission energy of the electrons from the cathode, this energy being expressed in volts. The time-interval during which the atom remains in the excited state, *i. e.*, during which the valency electron is in the $2p$ orbit, is not known with any degree of accuracy, as the direct experimental data are very meagre, and give no information as to whether this time-interval is the same for resonance as for other radiation. Kannenstine*, working with helium arcs, found that excited atoms could be detected as long as $2{\cdot}4 \times 10^{-3}$ sec. after the exciting voltage had been removed; and this must be the time during which the individual atoms persist in the excited state. It is probable, however, that this interval, as noted by Kannenstine, represents the time required for the resonance radiation to escape from the gas by a process similar to diffusion, and so this time-interval may represent the summation of the intervals for many thousands of absorptions and re-emissions of radiation.

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* *Ann. d. Phys.* xlix. p. 731 (1916).

† Phys. Rev. xx. p. 296 (1922).

It is also probable, as suggested by F. Horton and Miss A. C. Davies † as a result of their experiments with helium, that a second stage in the ionization may be brought about by the absorption of radiation from neighbouring impacts. If this second type of resonance radiation exists, and if it is capable of ionizing atoms already in the excited state owing to absorption of the first type of resonance radiation, it is to be expected that this effect would be more marked in completing ionization than impacts, for the same reason that radiation is more effective in displacing the valency electron to the $2p$ orbit than impacts. It appears that the complete ionization observed in low-voltage arcs, operated below the ionization potential, is accomplished mainly with the aid of the "photo-impact" effect.

In connexion with the spectroscopic study of low-voltage arcs in sodium and potassium vapours it was thought desirable to investigate the experimental conditions required for the production of such arcs.

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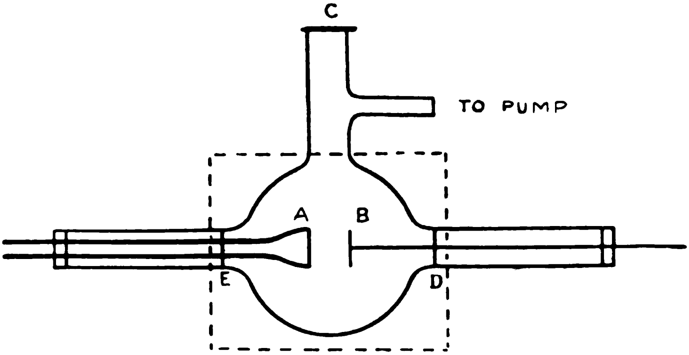
* Astrophys. Journ. lv. p. 345 (1922).

† Phil. Mag. xlii. p. 746 (1921).

2. *Experimental Arrangements.*

The form of tube which gave regular and consistent results is that shown in fig. 1. It was made of silica and had three branch tubes, one of which was used as a means of communication with a rotary oil-pump. A quartz plate C, waxed to the end of this branch, permitted visual observations of the emitted arc spectra. The anode B, a platinum disk whose plane was at right angles to the axis of the discharge-tube, was connected, electrically, to the pool of alkali metal placed at the bottom of the bulb by means of a short iron chain. It was found that such an arrangement assisted the maintenance of steady arcs once they had been started. The incandescent cathode A consisted of three lime-coated platinum strips or, in some experiments, three tungsten wires, arranged in parallel. In this manner a copious supply of electrons was emitted, using fairly heavy currents, without having an unduly large fall of potential across the ends of the incandescent filament. The lead-in wires, entering through ebonite plugs, were of iron and, having fairly large cross-sections, their resistances were practically negligible. These lead-in wires also passed through plates of glass E and D, which, fitting closely to the sides of the tube, minimized vapour condensation with its attendant liability to short-circuit the lead-in wires. The bulb, at the bottom of which was placed the metal, was heated by an electric furnace, the vapour in the discharge-tube being maintained at any selected temperature and pressure.

Fig. 1.



The negative terminals of the heating and anode voltage batteries were connected, and the potential difference between the hot cathode and anode, necessary to strike and maintain the arc, was measured by means of a voltmeter placed between B and the negative terminal of A, from which it will be seen that the readings obtained represented the maximum potential difference, and included any potential fall along the cathode.

In all experiments the distance between the platinum anode and the cathode was, approximately, 3 mm.

3. *Experiments with Sodium Vapour.*

With the cathode maintained at a definite and fixed temperature the voltage necessary to strike the arc gradually decreased as the furnace temperature, and so the vapour-pressure, increased. This was so whether tungsten wires or platinum strips were used, but in all cases the arcing potentials obtained with the tungsten filaments were slightly lower than those given with the platinum. This was due, probably, to the fact that it is impossible to heat platinum to such a high temperature as tungsten, and accordingly the number and speed of the emitted electrons are both greater with the tungsten. Some of the results obtained are shown in Table I., the filament in each set of experiments being intensely bright.

TABLE I.

Tungsten filament.

Furnace temperature.	Arc struck at	Arc maintained at
241° C.	8·2 volts.	7·8 volts.
315°	6·4	5·8
366°	5·8	5·1
426°	5·1	4·1
493°	4·0	2·9

Lime-coated platinum filament.

Furnace temperature.	Arc struck at	Arc maintained at
247° C.	10·5 volts.	10·1 volts.
312°	8·3	7·8
370°	7·1	6·5
428°	6·3	5·2
491°	5·4	4·1

As the filament temperature was raised, the potentials required to strike and maintain the arc decreased, which fact may be explained by the speed and number of the electrons emitted both increasing at the higher temperatures. The arc would start easily at 3·8 volts with the cathode intensely bright, the furnace temperature being 450° C., and this arc was maintained with 2·8 volts. It was possible, also, to strike the arc, after waiting 3 minutes, at 3·2 volts, but with lower potentials it would not start, even after waiting for several minutes. Very few readings could be taken with the filament at the high temperature necessary for such low potentials before the cathode fused and had to be renewed.

In another set of experiments a certain potential was applied which was not sufficient to start the arc. The filament current was then increased, and the value of this current noted when the arc became visible. The results obtained in this manner were not consistent.

Table II. gives the striking and maintenance potentials with various currents passed through tungsten filaments, the temperature of the furnace being 450° C. in every case.

TABLE II.

Filament current.	Arc struck at	Arc maintained at
10·4 amp.	4·3 volts.	3·1 volts.
9·9	4·9	3·8
9·3	5·4	4·5
8·5	5·9	5·2
7·9	6·5	6·0
7·0	7·1	6·7

The results given in Table III. show how the potentials, required for striking and maintaining the arc with the furnace at 275° C., depend upon the current passing through the tungsten filament.

TABLE III.

Filament current.	Arc struck at	Arc maintained at
10·3 amp.	6·2 volts.	5·2 volts.
9·9	7·0	6·2
9·3	7·9	7·1
8·6	8·9	8·2
7·8	10·0	9·5
7·1	11·3	11·0

It was observed that the establishment of the arc at any applied voltage was always followed immediately by a fall in potential between the electrodes. This effect has also been noted in other experiments by the author [*], and is similar to that which characterizes the electric discharge through gases at low pressures.

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[*] Phil. Mag. xliv. p. 946 (1922).

In all these experiments it was noted that the arc, once struck, increased in brightness as the potential difference was raised, but with very dense vapours this increased brilliancy was very marked, and, in addition, a bright continuous spectrum was superimposed upon the arc line-spectrum. This continuous spectrum was entirely absent at low vapour-pressures.

It is evident from the results given above that the vapour density and the filament temperatures are two of the main factors involved in the production of low-voltage arcs in sodium vapour, the applied potential decreasing as the filament temperature and vapour density are increased. It is possible to strike the arcs at voltages well below the ionization potential—5·1 volts—demanded by the quantum theory, but this can be explained by "photo-impact" ionization, which is likely to be particularly prominent under the conditions existing when these low-voltage arcs are obtained.

4. *Experiments with Potassium Vapour.*

Some experiments were also made with potassium vapour, a tube similar to the one shown in fig. 1 being used. The arcing potentials depended upon the filament temperature in a manner similar to that experienced with sodium vapour, but they were not quite as uniform and concordant, and the arcs, once struck, were not as steady as with sodium vapour.

With the tungsten filament at white heat and the electric furnace at 420° C., the arc in potassium vapour was started easily between 3·5 and 4·0 volts. It would then persist with a lower applied potential. As the vapour-pressure was decreased the voltages required for striking and maintaining the arc were more nearly equal, the difference between these two values becoming greater at higher vapour densities. The decreased potentials necessary to start the arc as heavier currents were passed through the tungsten filament are shown in Table IV., the furnace being maintained at 420° C.

Table IV.

Filament current.	Arc struck at	Arc maintained at
8·9 amp.	3·9 volts.	2·8 volts.
8·6	4·2	3·1
8·2	4·4	3·5
7·7	4·8	4·2
7·2	5·7	5·4

The striking potentials decreased as the vapour density was raised both with tungsten and lime-coated platinum filaments, but, as with sodium vapour, the potentials were always a little smaller with tungsten than with the platinum. Table V. shows the effect of increasing the vapour density, the tungsten filament in each case being intensely bright.

TABLE V.

Temperature of furnace.	Arc struck at	Arc maintained at
214° C.	7·6 volts.	7·2 volts.
280°	6·0	5·5
322°	5·3	4·7
356°	4·7	3·9
404°	3·8	2·7

5. *Conclusions.*

The potentials necessary to strike and maintain arcs in sodium and potassium vapours depend primarily upon the vapour density and the temperature of the cathode, the potentials decreasing as the vapour density and the cathode temperature both increase. The voltage required to maintain such arcs is always less than that on striking, but the difference between these two values becomes smaller as the vapour density is lowered. Arcs, struck and maintained with potentials less than the ionization potential of the vapour, are obtained with intensely hot cathodes, the ionization in such cases arising, probably, from the absorption of radiation emitted from atoms already excited but not ionized. Such ionization by "photo-impact" results in complete ionization of the vapour atoms by electrons, none of which have a velocity greater than that corresponding to the resonance potential.

The spectra of such low-voltage arcs have been investigated, and the results obtained will be communicated in another paper.

The author wishes to express his sincere thanks for a Government grant, through the Royal Society, which enabled him to carry out these investigations.

CVI. *On the Dielectric Constants of some Liquids, and their Variation with Temperature.* (Part I.) *By* G. Eric Bell, *B.Sc., and* Frank Y. Poynton, *B.Sc., Physics Research Laboratory, University College, Nottingham* [*].

Introduction.

INVESTIGATIONS on Dielectric Constant, and in particular its variation with temperature, have been the subject of several recent experimental researches. Theoretical work of Debye [†], Gans [‡] and others on the modification of the Clausius-Mosotti law have pointed to the possibility of obtaining from accurate measurements in this region considerable information with regard to the molecular structure of the dielectric.

Experimental Method.

The apparatus used consists essentially of two valve-maintained oscillatory circuits, which are in every case tuned so that the heterodyne note beats slowly with a third valve-maintained circuit oscillating at audible frequency.

If n_1 and n_2 are the frequencies of the two high-frequency oscillatory circuits, the frequency of the heterodyne-beat note is given by $n=n_1-n_2$, and if the frequency of the audible circuit is n', the beat-frequency observed in the telephones is given by $n-n'$.

The frequency of the valve-maintained circuits with the experimental condenser out is given, very approximately, by the relation

$$n=\frac{1}{2\pi\sqrt{L(C_0+C_1)}},$$

where C_0 is a constant depending on the distributed capacity of the circuit, C_1 is the capacity of the condenser, and L is the inductance in the circuit.

If the experimental condenser is put in the circuit, the frequency is given by

$$n=\frac{1}{2\pi\sqrt{L(C_0+C_1'+S)}}.$$

If C_1' is adjusted so that n remains constant, we have $S=C_1-C_1'$.

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[*] Communicated by Prof. E. H. Barton, D.Sc., F.R.S., F. Inst.P.

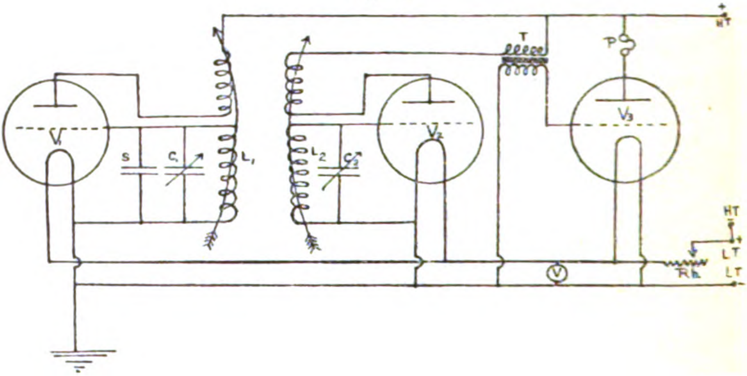
[†] P. Debye, *Physik. Zeitschr.* xiii. p. 97 (1917).

[‡] H. Isnardi u. R. Gans, *Physik. Zeitschr.* xxii. p. 230 (1921) & ix. p. 153 (1922).

Fig. 1 shows the arrangement diagrammatically. The coil L_1 together with the condensers C_1 and S in parallel constitute one oscillatory circuit maintained by the valve V_1. Similarly L_2 and C_2 form the second oscillatory circuit, maintained by the valve V_2. The transformer T and third valve V_3 form an amplifying unit, the advantage of which will appear later.

The audible frequency circuit is connected up exactly as the first oscillatory circuit, the condenser and coils being, of course, much larger.

Fig. 1.

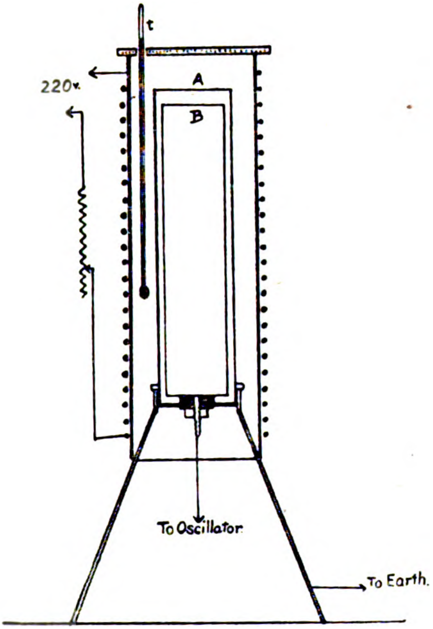


The coils used in the high-frequency circuits are duolateral coils wound on a two-inch former; by using coils having different numbers of turns, the frequency could be altered within certain limits, but over the small range which can be obtained in this way, the dielectric constant is practically independent of the frequency, so all the results have been obtained for one single frequency (of the order 4×10^7 cycles per second). C_1 is a Burndept "Low Loss" condenser, which is particularly suitable since it has good bearings and is efficiently screened from hand-capacity effects; C_2 is a Sullivan condenser, and S the "experimental condenser." The valves are Marconi-Osram R. 5v. and the transformer T by Pye's of Cambridge. The three circuits are all worked from the same H.T. battery, consisting of twenty-four large Leclanché cells, and also from the same L.T. battery, a 6-volt accumulator of very large capacity; a rheostat in the common L.T. + lead serves to reduce the voltage across the valve-filaments to the correct five volts, as indicated by a voltmeter connected permanently across the L.T. leads.

Experimental Condenser.

Several forms of experimental condenser have been tried, designed for use in large boiling tubes; it is found, however, much more convenient to make the outer plate of the condenser at the same time the containing vessel. The form finally adopted is shown in section in fig. 2. A is a brass cylinder about 18 cm. long, closed at one end; B is a second brass cylinder 15 cm. long, closed at both ends and mounted coaxially with the first. The inner cylinder is mounted and insulated from the outer one as shown in detail in fig. 3. Mica is used as an insulating washer since the temperature variation of its dielectric constant is practically zero[*].

Fig. 2.



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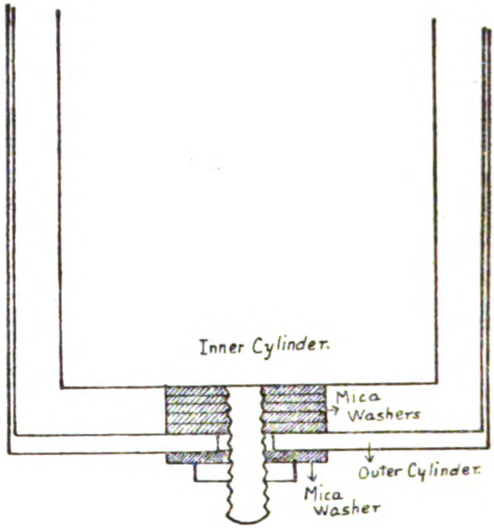
[*] See Dye and Hartshorn, Proc. Phys. Soc. xxxvii. (1924).

The capacity of the condenser, apart from the mica washer, is about 135 cm.

Fig. 3.



Heating Arrangements.

The lower end of the condenser fits into a ring supported on three legs. The temperature is controlled by means of a heating coil completely enclosing the condenser and supported on the same legs. A disk of asbestos board, with a hole to permit entrance of the thermometer, covers the top of the heating coil; this is found to ensure a more steady temperature being attained.

Details of Working.

Though the method is a simple one and capable of great accuracy, a number of precautions must be taken to ensure repeatable results. The whole apparatus with the exception of the experimental condenser and the batteries is contained in a large box, completely covered with tin-plate which is well earthed. The H.T. and L.T. batteries are contained in separate tin boxes also earthed. The leads from the experimental condenser, batteries, and phones are connected to suitable terminal boards at the back of the screened box. These earthed screens are necessary in order to eliminate external capacity effects and thus, in particular, to make the steadiness of the beat note independent of the movements of the observer. Apart, however, from such external screening, it is found very necessary to pay attention to several points in order to secure the requisite steadiness of the high-frequency oscillations. First, all contacts and condenser bearings etc. must be well made, and the whole apparatus protected from mechanical vibrations. Secondly, the L.T. accumulator must be of ample capacity, and even then steadiness cannot be obtained immediately after recharging. It would appear that the filament lighting is the main source of unsteadiness, and in this connexion we may note that there is considerable variation among the various types of valves, and after trials with a number we find Marconi Osram R. 5v. valves quite suitable for the purpose in hand. The low-frequency (audible) circuit keeps quite steady, as we have shown by comparison with tuning-forks. The amplifier permits the use of a loud-speaker which makes observation over long periods less tedious.

With regard to the arrangements for maintaining the experimental condenser at any given temperature, it is found that even after the thermometer has attained a steady state there is a slight drift of the beat note ; but since, after about an hour, this does reach a practically steady state, showing no variations capable of being measured on our compensating condenser, we feel confident that a state of thermal equilibrium persists in the heated enclosure, at the temperature given by the thermometer.

Results.

The results obtained for castor oil, olive oil, and linseed oil are given in the accompanying Tables and Curves. In each case a linear relation is found to hold between temperature and dielectric constant ; the dielectric constant at any temperature θ is related to that at 20° C. by the formula

$$K_\theta = K_{20}\left(1 - (\theta - 20)\,\alpha_{20}\right).$$

Values for α_{20} for the substance used are found to be :—

Castor Oil. $\alpha_{20} = \cdot 0015$.
Olive Oil. $\alpha_{20} = \cdot 0008$.
Linseed Oil. $\alpha_{20} = \cdot 0009$.

Table I.

Castor Oil.	
Temp. °C.	Diel. Cons.
17·5	4·86
57·2	4·50
68·5	4·36
100	4·20
121·5	4·05
144	3·82
161	3·76
185	3·56
a = ·0015	

Table II.

Olive Oil.	
Temp. °C.	Diel. Cons.
18·5	3·21
62·5	3·12
75	3·06
92·5	3·01
121	2·94
146	2·87
172	2·79
a = ·0008	

Table III.

Linseed Oil.	
Temp. °C.	Diel. Cons.
19	3·24
62·5	3·15
88	3·04
114	2·96
136	2·95
158	2·82
174	2·81
a = ·0009	

Fig. 4.—Temperature Variation of Dielectric Constant of Castor Oil.

a_{20} = ·0015.

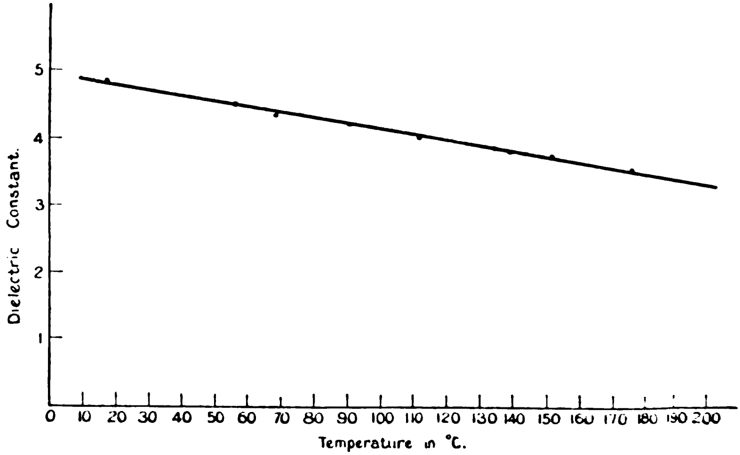


Fig. 5.—Temperature Variation of Dielectric Constant of Olive Oil.
$\alpha_{20} = \cdot 0008$.

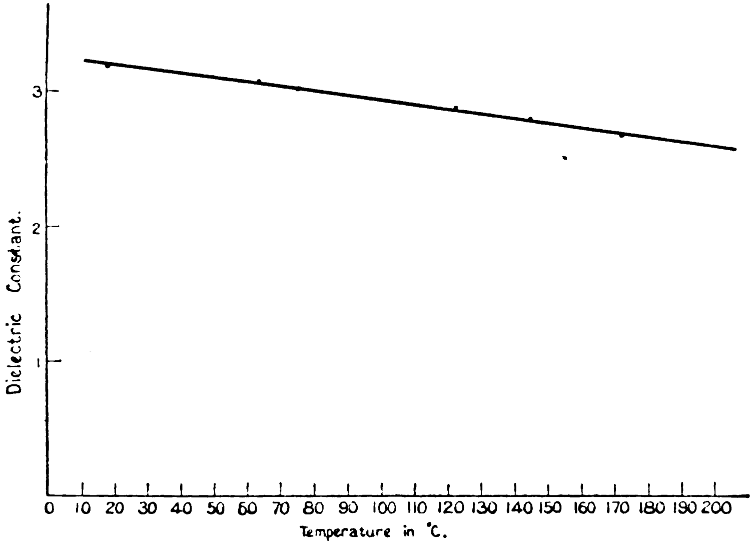
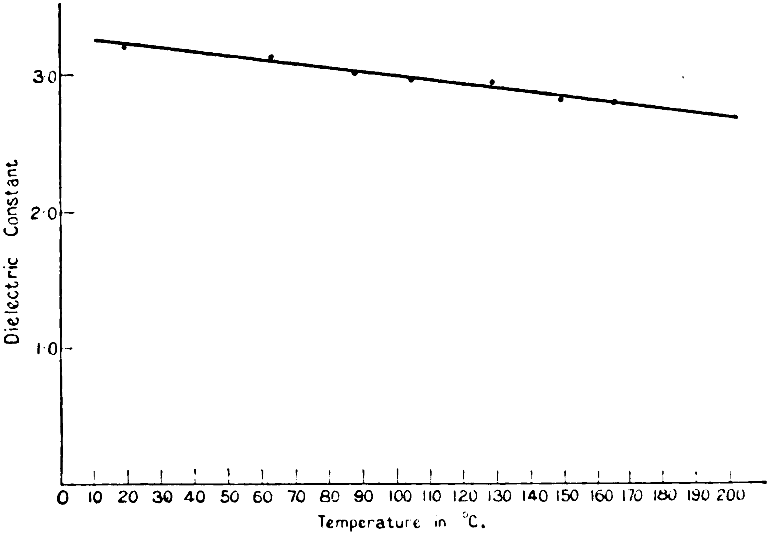


Fig. 6.—Temperature Variation of Dielectric Constant of Linseed Oil.
$\alpha_{20} = \cdot 0009$.



Summary.

In this paper an account is given of the application of valve-maintained oscillatory circuits to the measurement of the dielectric constant of castor oil, olive oil, and linseed oil, with special reference to its variation with temperature. A linear relation is found to hold in each case.

Some of the difficulties of working with valve-maintained oscillatory circuits and the precautions taken to ensure steadiness are discussed in some detail.

This work is being extended to other liquids, and also over greater ranges of temperature.

In conclusion, the authors wish to express their thanks to Prof. E. H. Barton, D.Sc., F.R.S., for his interest and help, to Mr. A. H. Franks, B.Sc., for assistance in constructing parts of the apparatus, and to the Department of Scientific and Industrial Research for a grant by the aid of which the research has been carried out.

Physics Research Dept.,
University College, Nottingham
February 5, 1925.

CVII. *A Generalization of the Theory of Artificial Lines.*

By The Research Staff of the General Electric Co., Ltd.
(*Work conducted by* A. C. Bartlett.) *

AN important class of electrical networks consists of artificial lines made up of numbers of symmetrical T or π sections, each section having 3 impedances elements of two different kinds. The theory of such lines can be expressed in terms of continued fractions of the form

$$a_1+\frac{1}{a_2+}\;\frac{1}{2a_1+}\;\frac{1}{a_2+}\;\frac{1}{2a_1+}\cdots\cdots$$

A more general class, which so far has not received attention, can be constructed which consists of a series of similar symmetrical sections, each of which is composed of $2n-1$ elements of n kinds. A typical member of this class of section is shown in fig. 1; the centre element may be either shunt or series.

The theory of this more general class which involves the use of continued fractions such as

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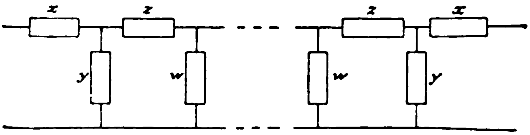
* Communicated by the Director.

$$a_1 + \frac{1}{\underset{*}{a_2}+}\,\frac{1}{a_3+}\dots\frac{1}{a_{n-1}+}\,\frac{1}{a_n+}\,\frac{1}{a_{n-1}+}\dots\frac{1}{a_3+}\,\frac{1}{a_2+}\,\frac{1}{\underset{*}{2a_1}}$$

can be readily developed by using certain theorems due to Muir relating fractions of this kind with Simple Continuants †.

Fig. 1.



If the impedances of x, z, etc. (the series elements) are a_1, a_3, etc. and of y, w, etc. (the shunt elements) are $\frac{1}{a_2}$, $\frac{1}{a_4}$, etc., then the impedance of an artificial line consisting of an infinite number of such sections (*i. e.* the Line Characteristic Impedance Z_0) will be given by the recurring continued fraction

$$Z_0 = a_1 + \frac{1}{\underset{*}{a_2}+}\,\frac{1}{a_3+}\dots\frac{1}{a_n+}\dots\frac{1}{a_2+}\,\frac{1}{\underset{*}{2a_1}},$$

which is equal to (Muir, *l. c.*)

$$\sqrt{\frac{K(a_1, a_2, a_3 \dots a_{n-1}, a_n, a_{n-1} \dots a_3, a_2, a_1)}{K(a_2, a_3 \;\dots\; a_{n-1}, a_n, a_{n-1} \;\dots\; a_3, a_2)}}$$

$$= \sqrt{\frac{K(a_1, a_2 \dots a_{n-1})\{K(a_1, a_2 \dots a_{n-2}) + K(a_1, a_2 \dots a_n)\}}{K(a_2, a_3 \dots a_{n-1})\{K(a_2, a_3 \dots a_{n-2}) + K(a_2, a_3 \dots a_n)\}}}.$$

The propagation constant θ can be determined by considering the impedance $Z_0 \tanh\theta$ of a single section short-circuited at the far end.

Thus

$$Z_0 \tanh\theta = a_1 + \frac{1}{a_2+}\,\frac{1}{a_3+}\dots+\frac{1}{a_n+}\dots+\frac{1}{a_3+}\,\frac{1}{a_2+}\,\frac{1}{a_1}$$

$$= \frac{K(a_1, a_2 \dots, a_n, \dots a_2, a_1)}{K(a_2, a_3 \dots, a_n, \dots a_2, a_1)}$$

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† 'Theory of Determinants,' 1882, chap. III.; also Proc. R. S. E. viii. pp. 229-236, and 'History of Determinants,' iii. p. 411 (1920).

of which the denominator is equal to

$$K(a_1, a_2 \ldots a_n)K(a_2, a_3 \ldots a_{n-1})$$
$$+K(a_1, a_2 \ldots a_{n-1})K(a_2, a_3 \ldots a_{n-2}).$$

Putting
$$K(a_1, a_2 \ldots a_n)=A_1,$$
$$K(a_1, a_2 \ldots a_{n-1})=B_1,$$
$$K(a_1, a_2 \ldots a_{n-2})=C_1,$$
$$K(a_2, a_3 \ldots a_n)=A_2,$$
$$K(a_2, a_3 \ldots a_{n-1})=B_2,$$
$$K(a_2, a_3 \ldots a_{n-2})=C_2,$$

then
$$Z_0=\sqrt{\frac{B_1(A_1+C_1)}{B_2(A_2+C_2)}},$$

$$\text{Tanh}\,\theta=\frac{\sqrt{B_1B_2(C_1+A_1)(C_2+A_2)}}{A_1B_2+B_1C_2}.$$

But A_1, B_1, C_1, A_2, B_2, and C_2 are connected by the relations

$$A_1B_2-A_2B_1=(-1)^n,$$
$$B_1C_2-B_2C_1=(-1)^{n-1},$$
$$A_1B_2+B_1C_2=A_2B_1+B_2C_1.$$

Whence it follows that Z_0 and $\tanh\theta$ can be put in the form

$$Z_0=\frac{B_1}{B_2}\sqrt{\frac{X}{X-2}} \text{ if } n \text{ is even}$$

$$=\frac{B_1}{B_2}\sqrt{\frac{X}{X+2}} \text{ if } n \text{ is odd ;}$$

$$\text{Tanh}\,\theta=\sqrt{1-\frac{1}{(X-1)^2}} \text{ if } n \text{ is even}$$

$$=\sqrt{1-\frac{1}{(X+1)^2}} \text{ if } n \text{ is odd,}$$

where $X=B_2(C_1+A_1)$.

This form has the advantage that, if all the elements are reactances, the frequency ranges over which the artificial line has zero attenuation can be determined.

For the condition is that θ shall be purely imaginary, and this is seen to require that X be real, and lie between 0 and $+2$ if n is even, and between 0 and -2 if n is odd.

To illustrate the general theory, we may apply it to the artificial line composed of π sections; here $n=3$, while

a_1 is zero. If the impedances of the series and shunt elements are u and v respectively, then

$$a_1=0,$$

$$a_2=\frac{1}{v},$$

$$a_3=u,$$

$$A_1=K\left(0,\ \frac{1}{v},\ u\right)=u,$$

$$B_1=K\left(0,\ \frac{1}{v}\right)=1,$$

$$C_1=0,$$

$$B_2=K\left(\frac{1}{v}\right)=\frac{1}{v},$$

$$X=\frac{u}{v},$$

whence

$$Z_0=\frac{1}{\frac{1}{v}}\sqrt{\frac{\frac{u}{v}}{\frac{u}{v}+2}}=\frac{uv}{\sqrt{u^2+2uv}},$$

and

$$\tanh\theta=\sqrt{1-\frac{1}{\left(\frac{u}{v}+1\right)^2}}=\frac{\sqrt{u^2+2uv}}{u+v},$$

these being the well-known standard formulæ.

CVIII. *Ultimate Rational Units.*

By NORMAN CAMPBELL, *Sc.D.*

PROF. LEWIS is quite mistaken. I am so little dissatisfied with my formal argument that, while it remains unchallenged, it seems to me waste of time to discuss the doctrine which it proves to be false.

CIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xlviii. p. 364.]

November 5th, 1924.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

Prof. **FRANZ XAVER SCHAFFER**, of the State Natural History Museum, Vienna, delivered a lecture on The History of the Vienna Basin, of which the following is an abstract:—

After the withdrawal of the sea from Central Europe in Upper Oligocene time the transgression of the Lower Miocene (First Mediterranean Stage) took place along a narrow channel between the foot of the Alpine-Carpathian range and the old Bohemian massif, the sea reaching a height of more than 500 metres above the present sea-level. This narrow channel, which is called the 'Extra-Alpine Basin,' then underwent subsidence, resulting in a fall in the level of the sea, during which the so-called Schlier and the beds of Grund were deposited. The latter strata contain the richest subtropical molluscan fauna known in Central Europe. But the appearance of freshwater beds associated with the deposits of this shallow sea shows the interruption of former marine communications towards the west and north.

During the First Mediterranean Stage the region within the Alps, where the 'Intra-Alpine Basin' is now situated, began to subside along two faults running obliquely to the strike of the folds, in a north-and-south and north-east and south-west direction. In the triangular depression between them a freshwater lake was formed, with its level at first higher than that of the sea without, but was finally invaded by the marine waters carrying a rich fauna (Second Mediterranean Stage). The sea attained a height at this time of about 450 metres above the present sea-level, and the subsidence of the floor of this shallow bay continued. A connexion existed at first with the Mediterranean across the Hungarian basin, Serbia, and the Balkan Peninsula, but in later Miocene time a considerable part of this sea was cut off, and an inland sea stretched from Vienna as far as Turkestan. This was the Sarmatian Sea, the brackish waters of which contained a very stunted and uniform fauna, and reached about 400 metres above sea-level.

Then mountain-folding took place in the Transylvanian Alps, and the large inland sea was divided into an eastern 'Pontic' and a western 'Pannonian' basin. The water-level of the latter rose to about 450 metres, the freshwater conditions became more accentuated, and the fauna still more impoverished (Pontic Stage = Lower Pliocene).

More than 700 metres of sediments were deposited in the Intra-Alpine Basin after the Second Mediterranean Stage, during continued subsidence of its floor. Then, by an outflow through the

'Iron Gate' near Orsova, a gradual but intermittent sinking of the water-level took place, in accordance with a similar intermittent lowering of the base-level of erosion in the eastern region. Shore-lines have been eroded on the borders of the basin at about 230, 200, 150, 100, and 50 metres respectively above the present river-plain. The predecessor of the Danube had its inflow on the site of the city of Vienna, and deepened its channels in accordance with the levels of the lake, depositing gravels over the terraces lying at the above-mentioned altitudes. With the deposition of the 50-metre terrace the sedimentation under lacustrine conditions came to an end, and the river eroded the soft sediments and cut lower terraces into them during Quaternary time. Of these terraces only one, that at 15 metres, is preserved within reach of the city of Vienna.

December 3rd, 1924.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

The following communication was read :—

'A Composite Dyke from Eastern Iceland.' By Miss Eileen Mary Guppy, B.Sc., F.G.S., and Leonard Hawkes, M.Sc., F.G.S.

The composite dyke cuts the Tertiary plateau-basalts of Breiddal (Eastern Iceland) and in its fullest development comprises seven members, dolerites alternating with quartz-porphyries, the central rock being porphyry.

It is shown that the acid members resulted from one intrusive act, which took place after the intrusions giving rise to the dolerites. From the disposition of the chilled phases it is inferred that the acid magma came up before the middle of the last-formed basic dyke had completely cooled, and an attempt is made to estimate the time which elapsed between the intrusion of the basic and that of the acid magma.

The acid rock is crowded with dolerite-xenoliths. These have a regular distribution, and it is suggested that they originated through the shattering of basic dyke-rock in some other place by explosive action, with incorporation of the fragments in the magma before intrusion into its present position.

The felspar-phenocrysts of the acid rocks are soda-orthoclases with a small optic axial angle, and have a weathered appearance which is ascribed to incipient melting. They are compared with the artificially melted felspars described by A. L. Day & E. T. Allen. Some of the longer felspars are curved, this being considered a mechanical effect due to the flowage of the viscous acid magma.

Xenocrysts of quartz and soda-orthoclase are irregularly distributed through the dolerites. They are similar to the phenocrysts of the acid rocks, and occur in the same relative proportions. It is suggested that their presence in the dolerites is due to the admixture of a small amount of phenocryst-bearing acid magma.

Evidence is cited to show the great viscosity of the acid magma.

Possibly it directly overlay a basic magma, which was intruded first because of its greater mobility, and with which small quantities of the overlying acid liquor were drawn off. The final episode was the uprise of the acid residuum with explosive action.

In an Appendix Prof. H. Hilton calculates the probable rates of cooling of the middle and periphery of a dolerite-dyke.

December 17th, 1924.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

Dr. JOHN DOWNIE FALCONER, M.A., F.G.S., Director of the Geological Survey of Nigeria, delivered a lecture on the Geology of Nigeria, illustrated by maps and lantern-slides. The lecturer said that the geology of Nigeria has been known in outline for the last ten or fifteen years; but systematic study dates only from the establishment of the Geological Survey in 1919. The Pre-Cambrian rocks consist of quartzites, schists, amphibolites, banded and granitoid gneisses, and foliated and partly foliated granites, pierced by tourmaline-pegmatites which are themselves in places foliated and in places tin-bearing, with the tinstone as a primary constituent. The latest component of the crystalline group is a Younger Intrusive Series, entirely non-foliated and ranging in composition from gabbro to granite, with the latter predominating. There is no evidence for assigning to this series any other than a Pre-Cambrian age. The succession has been from basic to acid, with intrusive rhyolites and quartz-porphyries immediately preceding the granite.

The Younger Granite is rich in soda, and exhibits both a biotitic and a riebeckitic facies, the latter usually local and marginal. After consolidation the granite was broken and fissured, and subjected to pneumatolytic alteration and mineralization, with the formation of tinstone, topaz, wolframite, blende, and pyrites. The older rocks adjoining the granite were also extensively fractured and broken, and subjected to similar alteration and mineralization contemporaneously with the granite. The pneumatolysis is marked by the complete absence of tourmaline, while tinstone is associated most abundantly with the alteration of the biotitic facies of the granite.

Nigerian tinstone is thus of dual age and origin. It occurs with tourmaline as an original constituent of the older pegmatites, and with topaz in the pneumatolytic modifications of the younger granite and surrounding rocks. The granite is by far the richer source, and has shed the larger part of the tinstone which is now being recovered from the alluvial deposits of the tinfields.

The sedimentary rocks of Nigeria consist of Cretaceous and Tertiary strata, separated by an unconformity. The former have been investigated in the vicinity of the Government colliery, and have been subdivided into four groups: the Lower Shales of marine origin, the Upper Shales of estuarine origin, the Coal Measures, and the Sandstone Group. These groups are in conformable succession, and, despite the occurrence in the Upper Shales of certain plants with Tertiary affinities, they are believed to represent accumulations of Cretaceous age from Turonian upwards.

The Tertiary rocks have been studied along the Eastern Railway between the coalfield and the sea, and have been subdivided into a lower sandstone group, an estuarine group with a middle Eocene fauna (Bende-Ameki Beds), a lignite group, and a group of unconsolidated sands and clays (Benin Sands). There is a well-marked unconformity between the Cretaceous and the Tertiary, and it is believed that the various groups of Tertiary rocks are also separated by unconformities. Fossiliferous Tertiary deposits have been located in other parts of Nigeria; but the classification established for the Eastern Railway cannot yet be extended to the other Tertiary areas.

The volcanic rocks of Nigeria have been investigated to some extent on the central tinfields, where an older and a younger group have been distinguished. Both are basaltic in character, and the older was subjected to considerable erosion before the effusion of the younger. Ancient river-beds with tin-bearing gravels occur beneath both groups of volcanic rocks.

January 7th, 1925.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

The following communication was read:—

'The Geology of the Rhobell Fawr District (Merionethshire).' By Alfred Kingsley Wells, M.Sc., F.G.S.

The area described covers some 30 square miles centred about the mountain-mass of Rhobell Fawr. The succession ranges from low down in the *Lingula* Flags to the Bala Mudstones.

The Cambrian rocks do not differ essentially from their equivalents in the Arthog—Dolgelley and Arenig—Moel Llyfnant districts, although the Tremadoc Beds are less completely developed, not extending far above the *Dictyonema* Band.

A feature of special interest is the development of an igneous cycle at a lower level than anywhere else in North Wales. The Rhobell Volcanic Group comprises an extrusive phase, the products of which were largely pyroclastic in origin and andesitic in composition; and a phase of minor intrusions when sills of hornblende-porphyrite and allied types were injected into the Upper Cambrian rocks in the neighbourhood of the volcanic centre, and dykes of similar composition penetrated the lower rocks of the Harlech Dome. The centre of eruption of which Rhobell is the denuded basal wreck, was a subaërial volcano which became active during the pre-Arenig interval. A further period of erosion was terminated by the transgression of the early Arenig sea, and the rocks of the Basement Group were deposited, these being derived from the denudation of a cone lying some distance east of Rhobell. The higher part of the Ordovician succession is condensed, the Lower Acid Volcanic Group of Cader Idris thins out in the south of the area, the zone of *D. bifidus* is feebly represented, and the *D.-murchisoni* Zone is probably absent. Fossils characteristic of the zone of *Glyptograptus teretiusculus* occur in mudstones at the base of the main volcanic series.

The Llandeilo Volcanic Group, the products of a submarine volcano, present many features of interest. Associated with thick felspar-crystal-tuffs are several flows of pillow-lava. The lowest is a normal basalt varying in texture from variolitic to doleritic, while the remainder are typical spilites. The andesitic magma of Arenig Mountain penetrated only into the extreme north of the area.

Unfossiliferous grey shales, the probable equivalents of the Llyn Cau Mudstones, were laid down during a period of normal sedimentation, during which the magma became more acid, so that the highest volcanic rocks, belonging to the Upper Acid Volcanic Group, include fragmental quartz-keratophyres. The active period of vulcanicity ceased finally and abruptly, the highest volcanic rocks being succeeded by a great thickness of Bala Mudstones.

Basic intrusions are common at several horizons between the Dolgelley Beds and the Upper Acid Group, and are without exception sills. The rocks range from gabbro through gabbroid dolerite, ophitic and subophitic dolerite, to porphyritic and spilitic types scarcely distinguishable from the basic lavas. They are believed to represent the phase of minor intrusions connected with the Llandeilo Volcanic Group. The area provides good illustrations of the action of an intrusive magma in persistently flooding certain horizons and invading selected rocks while leaving others unaffected.

As a consequence of its position at the south-eastern 'corner' of the Harlech Dome, the strike changes almost through a right-angle in passing from south to north. Folding along north-and-south axes is dominant, but the folds have been buckled against the Rhobell mass which acted as a resistant knot lying in advance of the hard core of the Dome. The area is much faulted, the most important dislocations being parallel to those recently described from the Bala district.

Complete chemical analyses of the chief rock-types have been made by Dr. H. F. Harwood.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

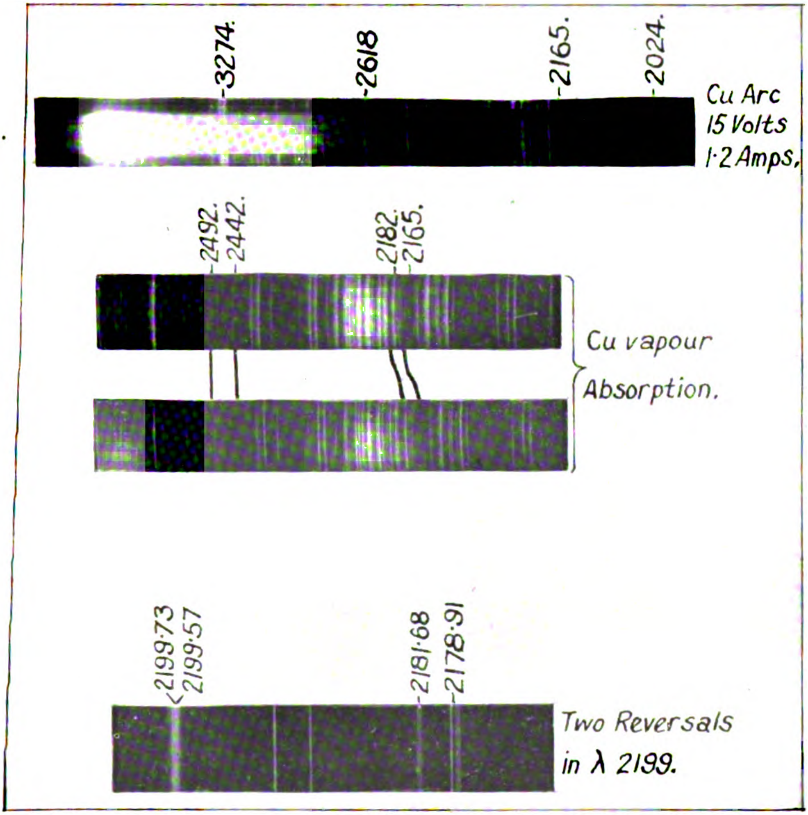
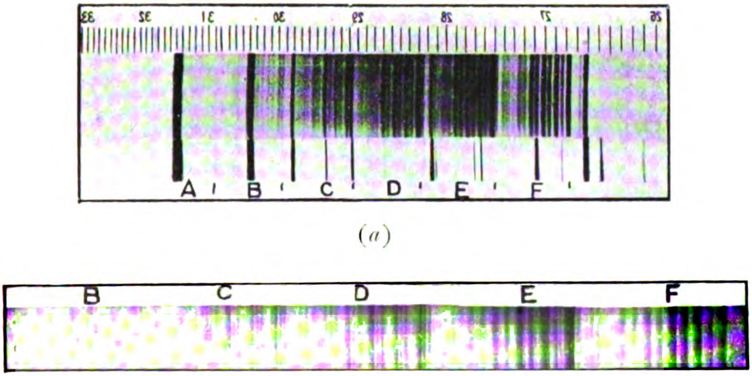

3274.
2618
2165.
2024.
Cu Arc
15 Volts
1·2 Amps.
2492.
2442.
2182.
2165.
Cu vapour
Absorption.
2199·73
2199·57
2181·68
2178·91
Two Reversals
in λ 2199.

FIG. I.



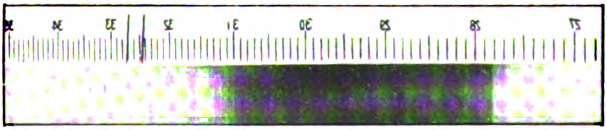
(*a*)

(*b*)

The Benzene Spectrum. TYPE I.

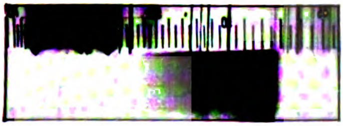
(*a*) Fluorescence spectrum (with Hg lines).
(*b*) Tesla-luminescence, large spectroscope without enlargement.

FIG. II *a*. TYPE II *a*.



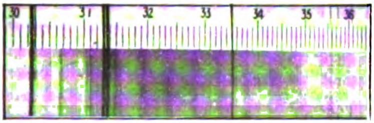
p-Xylene.

FIG. II *b*. TYPE II *b*.



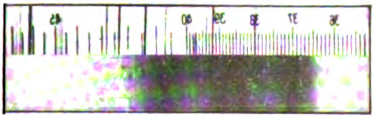
Hydrindene (visible region only).

FIG. III.



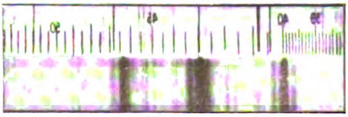
p-Toluidine.

FIG. IV. TYPE IV.



Anthracene.

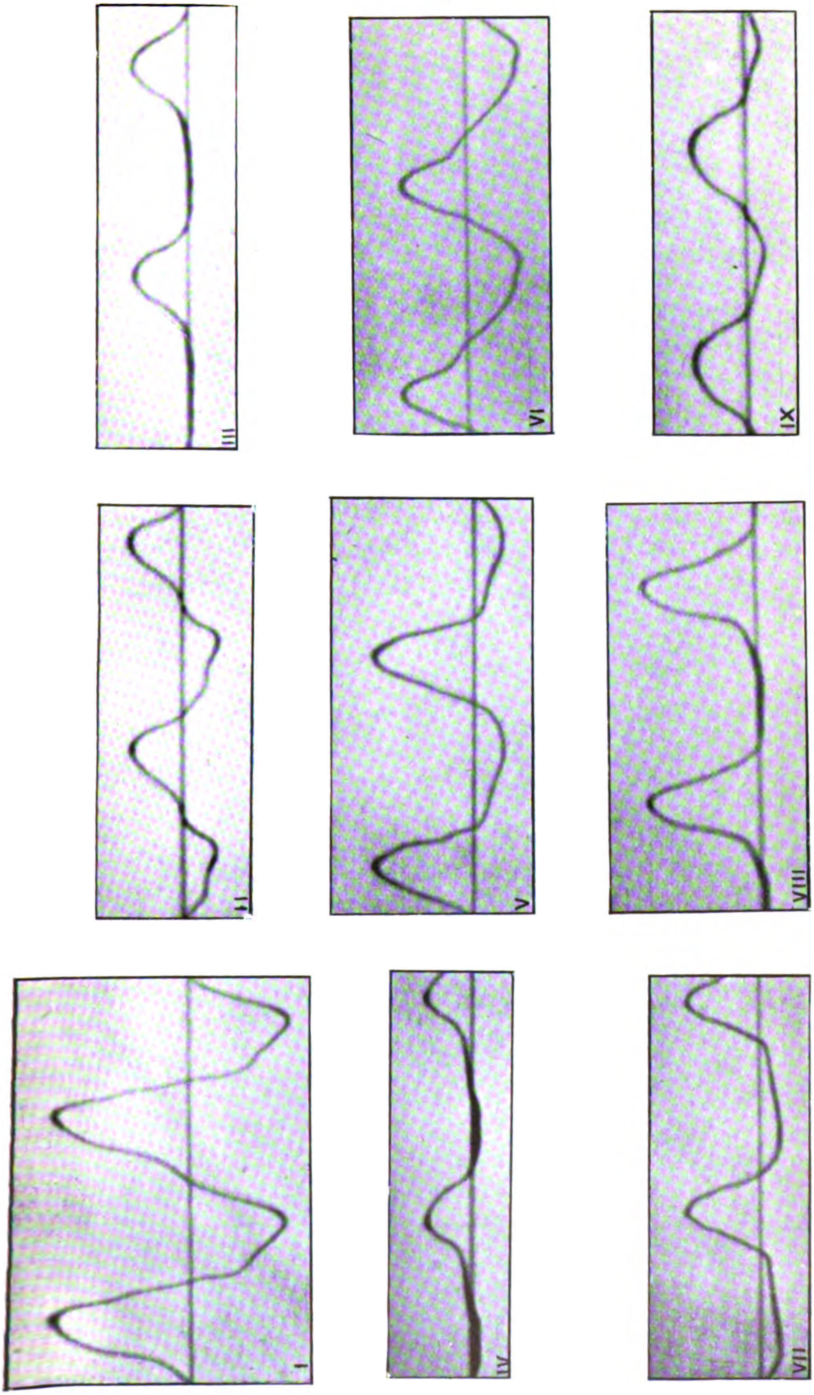
FIG. V. TYPE III.



Benzaldehyde.

Typical Emission Spectra.

Enlargements to nearly double size.



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[SIXTH SERIES.]

JUNE 1925.

CX. *On the Variation of the "Extinction" Voltages of certain types of Low Tension Discharge Tubes under Different Conditions.* By JAMES TAYLOR, *B.Sc.*, *A.Inst.P.*, *Pemberton Fellow*, and WILLIAM STEPHENSON, *B.Sc.*, *Armstrong College*, *Newcastle-on-Tyne* *.

ABSTRACT.

THE paper contains a description and theoretical discussion of results on the measurements of the extinction or lower critical voltages of "Osglim" lamps and certain types of air discharge-tubes, when a charged condenser is connected across the electrodes, and a "flash" takes place.

The method used for measurement is that described in a previous paper (Taylor and Stephenson, Journ. Scien. Instrs. ii. No. 2, p. 50).

The sequence of phenomena in the "flash" or discharge is analysed into three sections:—

(1) The capacity (C microfarads) charged to a potential of E volts, is placed across the tube, and a field of potential is thus set up across the tube electrodes, and a Townshend current flows through the latter. If a quantity of electricity q_1 is used up in establishing the glow, the potential V across the tube when the actual glow begins is given by

$$V = E - \frac{q_1}{C}.$$

---

* Communicated by Prof. G. W. Todd, M.A., D.Sc.

(2) The condenser discharges now through the tube (glow discharge) down to the lower critical voltage V_b^0. This lower critical voltage is given, on certain assumptions, by the relation,

$$V_b^0 = F + V_a',$$

where F is a constant and V_a' is the cathode fall of potential at the end of the "flash" period.

In cases where the full area of the cathode is employed in discharge, and the initial current is such as to give an abnormal cathode fall of potential,

$$V_a' = V_a + \phi(V, C),$$

where $\phi(V, C)$ is the "lag" of the cathode fall of potential at the end of the "flash" behind the normal cathode fall V_a. This becomes zero for normal current densities.

(3) At the end of the luminous period there is still a space-charge, etc. in the tube; this is cleared up, resulting in a quantity transference q_2 and a further reduction of the voltage across the condenser. We have therefore that the apparent lower critical voltage, as measured, is,

$$V_b' = V_b + \phi(V, C) - \frac{q_2}{C}.$$

It is shown that the experimental results are in general agreement with those predicted from theoretical considerations.

The least voltage required for production of a "flash" (for a capacity C across the discharge-tube electrodes) is shown to be given by

$$V_c' = V_c + \frac{q_1}{C},$$

where V_c is the normal sparking or upper critical potential.

Certain confirming experimental results for the "Osglim" lamp are given.

Introduction.

In a previous paper (Journ. Scien. Instrs. ii. No. 2, p. 50) the present writers put forward a method for the determination of the extinction voltages for low-tension discharge-tubes under different conditions of capacity and voltage across their terminals, and gave one or two illustrative results for the case of the neon lamp. In the investigation, a condenser of capacity C microfarads was charged to a potential E volts, and then connected across the terminals of a discharge-tube; a "flash" occurred, and the potential across the condenser at the end of the "flash", that is to say, the extinction or lower critical voltage under the conditions of experiment, was determined. It was pointed out that the determination of this extinction or lower critical voltage for a discharge-tube carrying a steady current is a matter of simplicity (Shaxby and Evans, Proc. Phys. Soc. Lond. xxxvi. p. 253, 1924). Recently, however, the phenomenon of "flashing" of discharge-tubes has received a certain amount of investigation (Pearson and Anson, Proc. Phys. Soc. Lond. xxxiv. p. 204, 1922; Taylor and Clarkson, Journ. Scien. Instrs. i. p. 173, 1923–1924; Proc. Phys. Soc. Lond. xxxvi. p. 269, 1924; Phil. Mag. xlix. p. 336, 1925), together with some of its applications in other directions (O. v. Baeyer and W. Kutzner, *Z. f. Phys.* xxi. p. 46, 1924; Appleton, Emmeleus, and Barnett, Proc. Cam. Phil. Soc. xxii. Pt. 3, p. 434, 1924).

The theoretically-derived expression for the time period of "flash" involves the lower critical voltage, but it is the value of this critical voltage under the obtaining conditions (in which a charged capacity is across the tube terminals) that is involved, *not* the lower critical voltage under a steady current. These critical voltages may differ considerably (see A. G. Tarrant, Proc. Phys. Soc. Lond. xxxvi. p. 280 (discussion), 1924; also Taylor and Stephenson, Journ. Scien. Instrs. *loc. cit.*).

The method employed in the present experiments is such that the lower critical voltage is determined under the actual conditions of a "flash" when a condenser of known magnitude, charged to a known potential, is connected across the tube.

The object of the present paper is to examine, in a more or less general theoretical manner, such condenser discharges and to put forward some results obtained in the cases of the "Osglim" lamp and air discharge-tubes.

Theoretical Investigation of the Variation of the Extinction Voltage V_b'.

One of us (Taylor) has put forward the following theoretical considerations of the problem:—

A condenser of capacity C microfarads is charged to a potential E volts, and is placed across the terminals of a low-tension discharge-tube. The following sequence of phenomena will occur and may be conveniently divided into three sections:—

(1) A field of potential across the discharge-tube electrodes will be established, and if there is any ionization within the filling gas a Townshend current will flow (*cp.* Reiche, *Ann. der Phys.* lii. p. 4, 1917). If the potential across the tube rises to the upper critical voltage or sparking potential V_c, under these conditions, the current will increase by ionization by collision, and a space-charge with its concomitant phenomena will be established.

Let i be the magnitude of the Townshend current at a time t secs. from the instant when the condenser was placed across the tube terminals, then the total expenditure of charge in establishing the negative glow is given by,

$$q_1 = \int_0^{t_0} i \, . \, dt,$$

where the integral is taken over the total time t_0 required to establish the glow. For a discharge-tube under constant conditions, and for capacities which are either fairly large (so that the whole of the cathode is covered with the negative glow) or of closely comparable magnitude, it would be expected that, for a constant ionizing agent (such as the γ-rays from radium bromide), q_1 would be approximately constant. It is evident, therefore, that the potential across the tube when the glow is just established is given by the relation,

$$V = E - \frac{q_1}{C} = E - \frac{\int_0^{t_0} i \, . \, dt}{C} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(2) The condenser now discharges through the tube down to the lower critical voltage $V_b{}^0$, that is, the voltage at which the tube ceases to conduct in the form of a glow discharge.

If we assume that the lower critical voltage $V_b{}^0$ is of the value of the cathode fall of potential plus a voltage just sufficient to carry the ions over from the negative glow to the anode, we may write (Taylor and Clarkson, Journ. Scien. Instrs. i. No. 6, p. 173),

$$V_b{}^0 = F + V_a{}', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $V_a{}'$ is the value of the cathode fall of potential at the end of the "flash" and F is a constant.

(3) At the end of the "flash" there is still a space-charge

and ionization in the gas within the tube. This space-charge, etc. will be cleared up very rapidly (in a time of the order of 10^{-6} sec.), but in the process there will have been a definite transference of electrical charge across the tube, and a further depreciation of the voltage across the condenser. Let this quantity be denoted by q_2, and we have,

$$q_2=\int_0^{t'} \mathrm{I}\,.\,dt,$$

where I is the instantaneous current at a time t seconds after the termination of the luminous discharge, and t' is the time required for the space-charge, etc. to be cleared up. The further diminution of the voltage across the capacity C is evidently

$$\frac{q_2}{\mathrm{C}}=\frac{\int_0^{t'} \mathrm{I}\,.\,dt}{\mathrm{C}},$$

so that the apparent lower critical voltage for the tube under these conditions is given by

$$\mathrm{V}_b{}'=\mathrm{V}_b{}^0-\frac{\int_0^{t'} \mathrm{I}\,.\,dt}{\mathrm{C}}=\mathrm{V}_a{}'+\mathrm{F}-\frac{\int_0^{t'} \mathrm{I}\,.\,dt}{\mathrm{C}}, \quad . \quad (3)$$

$\mathrm{V}_a{}'$, F, and q_2 are complicated functions.

Further Consideration of Section (1).

It was shown that for the glow-discharge to be produced a quantity of electricity q_1 was transferred across the tube, and that the potential across the condenser after this transference was given by the relation of equation (1). Now, if $\mathrm{V}<\mathrm{V}_c$ (the upper critical voltage), which we are assuming to be a constant, no glow-discharge can be produced. We have evidently for a "flash" just to take place,

$$\mathrm{V}_c=\mathrm{E}-\frac{\int_0^{t_0} i\,.\,dt}{\mathrm{C}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When the value of the capacity C is great (in these experiments usually of the order of 10^{-3} microfarad or more), the minimum value of E necessary for a glow-discharge to be produced is, within the limits of experimental error, of the value V_c, since the second term of equation (4) is small compared with the first, for large capacities. When, however, C becomes small (10^{-3} microfarad and less in most experiments on "Osglim" lamps), the second term increases fairly rapidly, and the minimum voltage across the condenser required for a glow-discharge to be produced is given by

$$V_c' = V_c + \frac{\int_0^{t_0} i \, . \, dt}{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If we can assume for these small values of C that the integral term of equation (5) is constant, it is evident that the graphs showing the relationship between V_c' and C will be hyperbolic in form. This is found to be approximately correct in experiments on the neon discharge-tubes.

Further Consideration of Section (3).

There are two cases to be distinguished :

(*a*) Where the current at the commencement of the luminous period is sufficiently great to give abnormal cathode falls of potential (H. A. Wilson, Phil. Mag. ser. 6, iv. p. 608, 1902).

(*b*) Where the current at the beginning of the "flash" is such as to give the normal cathode fall of potential (Wilson, *loc. cit.*). In the case of small capacities, a portion only of the cathode area is utilized in the luminous discharge, so that the current density may still be of the normal value.

Under the first heading is included the discharge through a tube when large capacities are employed, but it must be observed that the fact of abnormality of the cathode fall of potential is conditioned by the size of the cathode as well as by the magnitude of the capacity.

Let the cathode fall of potential be V_a^0 at the beginning of the "flash". The potential across the tube falls rapidly (the whole "flash" occupying a short fraction of a second only, as a rule), and there will be a "lag" of the cathode fall behind the normal value that would be attained if a sufficient time were allowed to elapse. (One may regard this "lag" as a "fatigue" or hysteresis effect.)

We may write, therefore, on certain assumptions (see Taylor and Clarkson, Journ. Scien. Instrs. *loc. cit.*),

$$V_b' = V_a' + F,$$

where V_a' is the value of the cathode fall of potential when $(V - V_a') = F$, the voltage just sufficient to carry the ions over to the anode from the negative glow. V_a' will be some function of i, the initial current through the tube in the luminous period, and will thus depend largely upon V (see equation (1)) and the magnitude of C (see also Taylor and Clarkson, Phil. Mag. *loc. cit.*), so that we may write

$$V_a' = V_a + \phi(V, C),$$

where V is the voltage across the tube at the instant the glow-discharge begins. We have, further, from equation (3),

$$V_b' = V_a + F + \phi(V, C) - \frac{\int_0^{t_1} I \, . \, dt}{C}$$

$$= V_b + \phi(V, C) - \frac{\int_0^{t_1} I \, . \, dt}{C}, \quad . \quad . \quad . \quad . \quad (6)$$

where V_b is the normal lower critical voltage (that is, the lower critical voltage when $V_a' = V_a$).

Now, when C is large, the last term of equation (6) is of negligible value compared with the others, so that the equation may be approximated to the form

$$V_b' = V_b + \phi(V, C). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

When the value of the capacity C becomes such that the current through the discharge-tube never rises above the normal density value, the "lag" $\phi(V, C)$ becomes zero, we have $V_b' = V_b$, and the lower critical voltage should be independent of C over a wide range.

For smaller capacities the last term of equation (6) comes into prominence, and we have the following approximate relation holding :—

$$V_b' = V_b - \frac{\int_0^{t_1} I \, . \, dt}{C}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

THE EXPERIMENTAL RESULTS.

Introduction.

A number of experiments were carried out using neon discharge-tubes in the convenient form of the well-known "Osglim" lamps. These lamps contain a filling-gas of about 75 per cent. of neon and 25 per cent. of helium (together with certain impurities, such as hydrogen and mercury vapour), at a pressure of approximately 10 mm. of mercury. The electrodes are of iron, the cathode being in the form of some letter of the alphabet (or a "beehive" spiral of iron wire, in one type of the lamp), and the anode a small cylinder of iron, at a distance of one or two mm. from the cathode. There is no positive column in the discharge of these lamps, the light being emitted entirely from the negative glow (Ryde, Phot. Journ. June 1922).

In the experiments on the air discharge-tubes, a "beehive" "Osglim" lamp was improvised as a discharge-tube, by opening the nipple of the bulb and sealing on a glass tube so that the lamp could be attached to a Toepler pump and apparatus for evacuating. Phosphorus pentoxide tubes were employed for drying the air and the pressure was measured by a McLeod gauge.

In other experiments on the air discharge-tubes, a tube with parallel molybdenum-wire electrodes was used. This tube was the one used in experiments on the critical resistance for "flashing" of air discharge-tubes, described in a previous paper (Taylor and Clarkson, Phil. Mag. *loc. cit.*), where a description of the tube is given.

Previous to experimenting, the tubes were "overrun" so as to bring them into a more stable condition (Taylor and Clarkson, Phil. Mag. *loc. cit.*; also *cp.* Dubois, *C. Rend.* clxxv. p. 947, 1922), and overcome the trouble caused by "salient" points on the electrodes.

The Prevention of "Lag" in "Flashing."

The time "lag" in the occurrence of a discharge, behind the voltage tending to produce it, is a well-known phenomenon. In the present experiments a quantity of radium bromide in a sealed glass tube was used as external ionizing agent (the γ-rays being the effective ionizing radiations) (Taylor and Stephenson. Journ. Scien. Instrs. *loc. cit.*) to overcome the "lag" effects. In the case of the larger capacities (about 10^{-1} microfarad upwards) the value of the lower critical voltage, as determined experimentally, was found to be independent of the quantity of the radium bromide or its distance away from the tube, provided there was sufficient ionization produced to do away with the "lag." For the small capacities the results appeared to be independent of the quantity and distance of the radium bromide, but it was most difficult to get a discharge at all unless the radium bromide was in close proximity to the tube, and without its presence definite values of V_b' were not obtainable.

An interesting observation was made when using the parallel molybdenum-wire electrode discharge-tube. With capacities of the order 10^{-3} microfarad and certain charging voltages, a discharge could be obtained when the radium bromide was removed to some distance, but when it was brought into close proximity to the tube no discharge could be obtained, the condenser charge being dissipated, presumably, by the "dark" discharge which precedes the luminous one.

Nature of the "Flashes."

In the "Osglim" lamps the full area of the cathode is employed in the discharge, for capacities greater than some 0·05 microfarad (this value varies somewhat, of course, with the type of lamp); but the intensity of the negative glow at the lower limits is exceedingly feeble. The intensity increases with the capacity C, and becomes very great for large capacities. In the case of the small capacities a part only of the cathode is illuminated by the negative glow during the luminous period. At values of C of the order of 10^{-4} microfarad a very minute portion of the cathode is utilized, and it is most difficult under such conditions to judge whether the type of discharge is normal.

When using the molybdenum-wire electrode tube, the full area of the electrode was employed down to very small capacities (about 0·004 microfarad), but the intensity of the glow decreased as the capacity diminished.

Abnormal Types of Discharge.

Several abnormal types of discharge were observed in the "beehive" air discharge-tube. Occasionally a "salient" point would crop up on the anode, and the discharge would be concentrated there as a sort of positive or anode glow, the intrinsic luminosity of the region of the "salient" point being very much greater than that of the usual negative glow. This type of discharge borders upon the arc discharge, and the value of the lower critical voltage V_b' is very much less than the normal, though precise determinations cannot be made because of the erratic nature of the discharge.

Further, in the case of the same tube at the lower pressures investigated (less than about 1 mm. of mercury), in some "flashes," instead of the usual diffuse negative glow a more intense discharge immediately around the anode was produced. Occasionally streamers from the anode were observed.

These abnormal types of discharge appear to be similar to some of those observed by Watson in neon and helium discharge-tubes (Proc. Cam. Phil. Soc. xvii. p. 90, 1913).

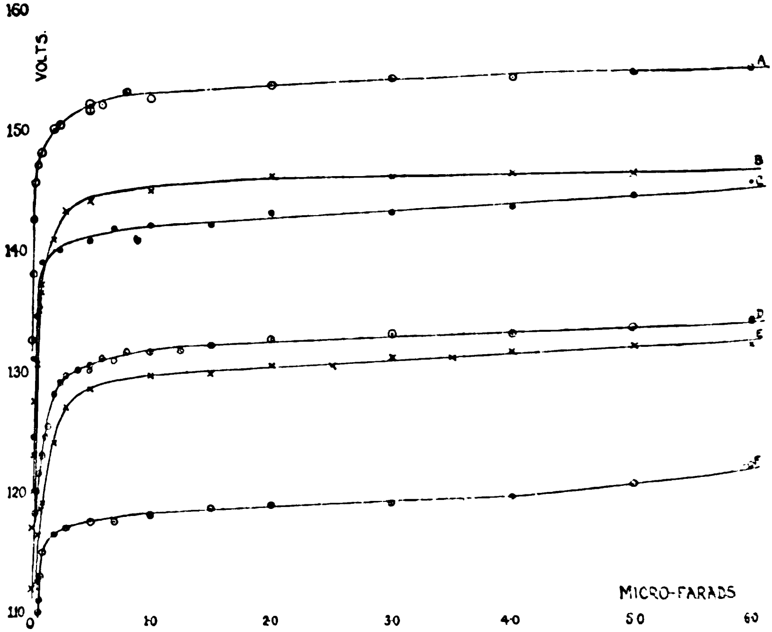
THE EXPERIMENTAL RESULTS FOR THE NEON DISCHARGE TUBES.

The Variation of the Lower Critical Voltage with the Capacity for a Fixed Charging Voltage.

The variation of the lower critical voltage with the capacity for fixed charging voltages was investigated in the case of a number of types of the "Osglim" lamps. The general relations obtained were the same for all the different types.

The graphs of fig. 1 show the relations between the lower critical voltage V_b' and C for fixed charging voltage of

Fig. 1.—Graphs showing the Relationship between the Lower Critical Voltage and the Capacity for a Fixed Value of the Charging Voltage E.



Graph A.—"Osglim" lamp, "R" type. Not "overrun." External ionizing agent, radium bromide.

Graph B.—Do. after "overrunning."

Graph C.—"Osglim" lamp, "O" type. Not "overrun." External ionizing agent, radium bromide.

Graph D.—"Osglim" lamp, "R" type. "Overrun." External ionizing agent, radium bromide.

Graph E.—"Osglim" lamp, "Beehive" type. "Beehive" as cathode. External ionizing agent, radium bromide.

Graph F.—Do. "Beehive" as anode.

Charging Voltage E, 200 volts throughout.

TABLE I. (Graphs of fig. 1.)

Graphs showing Relationship between Lower Critical Voltage and Capacity, for a Fixed Value of the Charging Voltage E (200 volts).

Capacity in μF.	(A.)	(B.)	(C.)	(D.)	(E.)	(F.)
7·25	...	...	146	136	132	122·5
6·0.........	155	...	145·5	134	132	122
5·0.........	154·5	148·3	144·5	133·5	132	120·5
4·0.........	154	146·3	143·5	133	131·5	119 5
3·5.........	...	...	...	...	131	...
3·0.........	154	146·0	143	133	131	119
2·5.........	...	...	...	...	130·3	...
2·0.........	153·5	146·0	143	132·5	130·3	119
1·5.........	...	...	142	132	129·7	118·5
1·25	...	...	...	131·5	...	...
1·0.........	152·5	144·8	142	131·5	129·5	118
0·8.........	153·0	...	...	131·5	...	...
0·75	...	...	141·5	130·7	...	117·5
0·6.........	152·0	...	...	131	...	...
0·5.........	152·0(151·5)	143·8	140·7	130	128 5	117·5
0·4.........	...	...	...	130	...	...
0·3.........	...	143·2	...	129·5	127	117
0·25	150·3	...	140	129	...	...
0·2.........	150	140·8	...	128	124	116·5
0·154......	...	...	...	125·5	...	...
0·135......	...	...	...	124·5	...	...
0·10	148	137·2	139	123	119	115
0·083......	148	136·5	...	...	118·5	113
0·071......	147	135	...	121·5	116·5	111
0·063......	...	130·5	134·5	120·9	...	110
0·05	...	...	134	120	...	...
0·046......	145·5	130·5	...	118·2	112·5	...
0·0315 ...	142·5	127·5	131	...	...	...
0·016......	138	123·0	124·5	...	...	...
0·014......	...	120	...	...	...	...
0·008......	132·5	115	...	...	...	...
0·005......	...	112	...	...	...	...

(A.) "R_1" lamp. Not overrun. RaBr external ionizer.
(B.) do. After overrunning. RaBr external ionizer.
(C.) "O" lamp. Not overrun. RaBr; lamp in complete darkness.
(D.) "R" overrun lamp. RaBr.
(E.) "Beehive" lamp. Beehive as cathode.
(F.) do. do. anode.

200 volts, and several types of lamps (the description of the lamps is given in the fig.).

The following general results are apparent from a consideration of the graphs :—

(1) For large capacities above about 1 microfarad or so the graphs are approximately linear in C.

These portions of the graphs may be expressed by the general empirical relation,

$$V_b' = V_b + \beta . C, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where β is some small constant for a fixed value of the charging voltage E.

(2) With capacities less than about 1 microfarad, the slope of the graphs begins to increase, at first slowly, and then quickly, and V_b' decreases rapidly as C is diminished. This is to be expected from equation (8). It is not possible, however, to treat this portion of the curves quantitatively, because the function $\int_0^{t'} I . dt$, which represents the quantity transference across the tube by the clearing up of the space-charge, etc., is certainly not constant for all capacities, for it is found, experimentally, that the intensity of the glow decreases with the capacity, and the actual area of cathode employed in discharge begins to diminish with the smaller capacities.

The function $\int_0^{t'} I . dt$, need not be more than some 10^{-6} practical units, a value well within the probabilities of the case, to explain the magnitude of the V_b' variations.

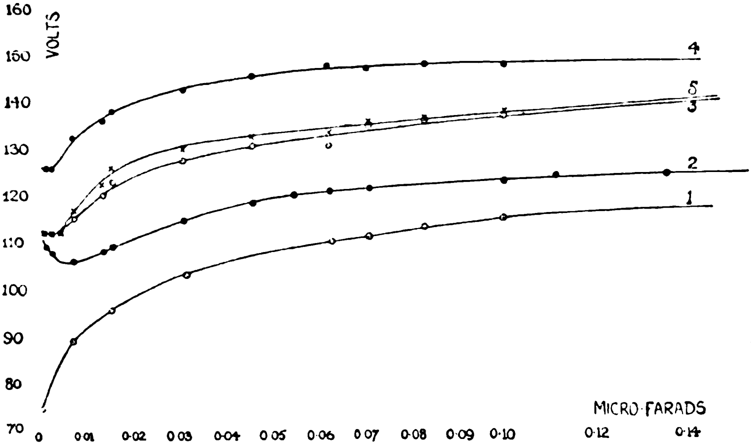
Fig. 2 shows the similar relations for the smaller capacities (magnified capacity scale). It is observable that, except in the case of graph 1 where the cathode area is very small, the lower critical voltage attains a minimum at very small capacities, and appears to rise in value with further diminution of C. (It was sometimes difficult to decide whether V_b' was actually rising or merely stationary at these small capacities.)

The minima of the graphs suggests that the ratio

$$\frac{\int_0^{t'} I . dt}{C}$$

attains a maximum and then decreases as C is further diminished.

Fig. 2.—Graphs showing the Relationship between the Lower Critical Voltage and the Capacity for a Fixed Value of the Charging Voltage E, for small Capacities.



Graph 1.—"Beehive" "Osglim" lamp. Not "overrun." Neon lamp used as external ionizing agent. "Beehive" as anode, Full cathode is used in discharge throughout, but intensity is very feeble for the smaller capacity values.

Graph 2.—"Osglim" lamp, "R" type. "Overrun." Radium bromide used as external ionizing agent. Less than full cathode used for capacities less than 0·04 microfarad (circa).

Graph 3.—"Osglim" lamp, "R" type. "Overrun." Radium bromide used as external ionizing agent. Full electrode used till about 0·01 microfarad.

Graph 4.—"Osglim" lamp, "R" type. Not "overrun." Radium bromide used as external ionizing agent.

Graph 5.—"Osglim" lamp. Same lamp as (4), but slightly "overrun." Radium bromide used as external ionizing agent.

Charging Voltage throughout, 200 volts.

Table II. (Graphs of fig. 2.)

Neon Lamp, Small Capacities.

Neon Lamp. E = 200 volts constant.

Graph 1.

"Beehive" lamp; not "overrun." Neon "I" lamp used as external ionizing agent; steady temperature condition. The small anode is used as cathode. E = const. 200 volts. Whole cathode is used throughout; discharge very feeble, however, for lowest capacity value.

Results :—

C =	0·1 μF	0·083	0·071	0·063	0·046
V_b' =	115	113	111	110	107

C =	0·032 μF	0·016	0·077	0·001
V_b' =	103	95·5	89	74

Graph 2.

"R" aged lamp. RaBr as external ionizing agent. E = 200 volts.
Not all the cathode is used at capacities less than 0·04 (circa).

$C =$	0·154 μF	0·135	0·111	0·071	0·062
$V_b' =$	125·5	124·5	124·5	121·5	121·0
$C =$	0·055 μF	0·046	0·0315	0·016	0·0142
$V_b' =$	120	118·2	114·5	109·0	108·0
$C =$	0·0077 μF	0·0033	0·0022		
$V_b' =$	106	108	109		

Graph 3.

"R_2" lamp. After "overrunning." E=200 volts. RaBr.
Compare with 4 (below). Full electrode employed until 0·016 μF.

$C =$	0·1 μF	0·083	0·071	0·062	0·0462	0·0315
$V_b' =$	137·2	136·5	135	130·5	130·5	127·5
$C =$	0·016 μF	0·0147	0·0077	0·0056	·0033	
$V_b' =$	123	120	115	112	112	

Graph 4.

"R_2" lamp. Before "overrunning." E=200. RaBr.

$C =$	0·1 μF	0·083	0·071	0·062	0·0462	0·0315
$V_b' =$	148	148	147	148	145·5	142
$C =$	0·016 μF	0·0147	0·0077	0·0033	0·0022	
$V_b' =$	138	136	132·5	126	126	

Graph 5.

"R_2" lamp. RaBr ionizing agent. E=200. Slightly "overrun."

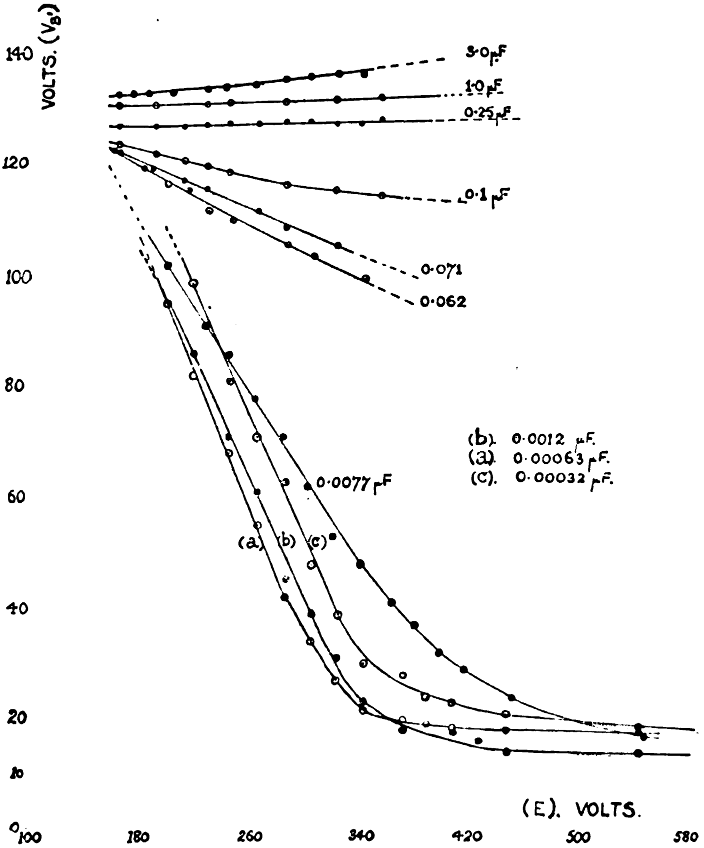
$C =$	0·1 μF	0·083	0·071	0·062	0·0462	0·0315
$V_b' =$	137·2	136·5	135·5	133	132·2	130
$C =$	0·016 μF	0·0147	0·0077	0·0033	0·0022	
$V_b' =$	123·5	122	117	112	112	

From equation (1) we see that V, the voltage across the discharge-tube at which the glow discharge begins, becomes less as C is decreased. It is found experimentally (see later) that the divergence of V from E only becomes grave at values of C of the order of 10^{-3} microfarad, consequently, since the the magnitude of the current at the commencement of the glow-discharge depends on V, the current magnitude will begin to fall off rapidly with diminution of C at capacities of the above order: concurrently, the area of the negative glow will diminish, thus diminishing the quantity transference in clearing up the space charge, etc. The above ratio may thus achieve a maximum and begin to decrease, so that, as is to be seen from a consideration of equation (8), V_b' may increase again as the capacity becomes smaller.

The Variation of the Lower Critical Voltage with the Charging Voltage E *for Fixed Values of the Capacity.*

Fig. 3 gives a set of graphs showing the relationship between the lower critical voltage V_b' and the charging voltage E, for fixed values of the capacity C. The lamp used was an “Osglim” lamp of the letter “R” type.

Fig. 3.—Graphs showing the Relationship between the Lower Critical Voltage and the Charging Voltage E, for Constant Values of the Capacity C.



“Osglim” lamp. “R” type. “Overrun.”

or small capacities (*a*, *b*, *c*, etc.) only a small part of the cathode is used, except at 500 volts or more when the total area of the cathode is covered with negative glow during the discharge.

From theoretical considerations, we saw that the general form of these curves is given by the relation of equation (6). This was approximated to equation (7) for large capacities, and to equation (8) for the smaller capacities.

The graphs for the higher capacities (0·25 microfarad and above) are approximately linear. It would appear, consequently, that the "lag" effect, represented by the function $\phi(V, C)$ is approximately linear in E [in these cases $V=E$, of course].

For the small capacities, curves in general agreement with what might be expected from equation (8) are obtained. At high charging voltages, however, V_b' appears to attain a constant minimum value. This may be due to the numerator of the second term of equation (8) attaining a maximum constant value; that is to say, that when E has attained a sufficiently high value the quantity transference due to the clearing up of the space charge and negative glow, etc., is constant, but, on the other hand, certain results appear to suggest that it may be the ionizing potential of the filling-gas of tubes. Much work is required before anything definite can be said on the subject.

TABLE III.

Variation of V_b' with E (C constant).

C.	E.	V_b'.	C.	E.	V_b'.	C.	E.	V_b'.
3μF	343	137	1·0μF	357	133	0·25μF	357	129
	325	137		342	...		342	128
	305	136·5		324	132·5		324	128
	287	136·0		305	132·3		305	128·4
	265	134·7		287	132·0		287	128·4
	243	134·2		267	131·8		267	128
	232	134·0		246	131·8		246	128
	221	133·6		230	131·2		230	127·6
	205·5	133·3		213	131·2		213	127
	186·5	133·2		192	131·0		192	127
	176	133·0		170·5	131·0		165	127
	165·6	132·9		165·0	131·0			
0·1μF	357	115	0·071μF	324	106	0·062μF	345	101
	324	116		287	109		308	104
	287	117		267	112		288	106
	246	119		230	116		248	[illegible]
	230	120		213	117·5		231	112
	213	121		190	119·5		217	[illegible]
	192	122		166	122·5		201	[illegible]
	165	124					184	[illegible]
							163	[illegible]

TABLE III. (*continued*).

0·0077 μF	201	102	0·00063 μF	201	95	0·0012 μF	201	95
	229·5	91	(*a*)	220	82	(*b*)	220	86
	246	86		246	68		246	71
	265	78		267	55		267	61
	285	71		287	42		287	45
	304	62		306	34		306	39
	322	53		324	27		324	31
	342	48		344	21·5		344	23
	365	41		373	20		373	18
	382	37		390	19		390	...
	399	32		409	18·5		409	18
	417	29		428	...		428	16
	452	24		448	18		448	14
	549	17		545	17·8		545	14

C.	E.	V_b'.
0·00032 μF	220	98
(*c*)	246	81
	267	71
	287	63
	306	48
	324	39
	344	30
	373	28
	390	24
	409	23
	428	...
	448	21
	545	18·5

GENERAL.

"R_1" lamp —For small condensers (*a*, *b*, *c*, etc.) only a small part of the electrode is used, except at 500 volts or more, when nearly the whole cathode becomes covered with glow during the discharge.

Variation of V_c' *with the Capacity* C.

It was shown that the minimum charging voltage across the capacity, required for a glow-discharge to be produced, was given by the relation of equation (5). Fig. 4 shows the graphs obtained in the cases of two neon discharge-tubes. The graphs are approximately hyperbolic, graph (*a*) being represented by the empirical form (approximately)

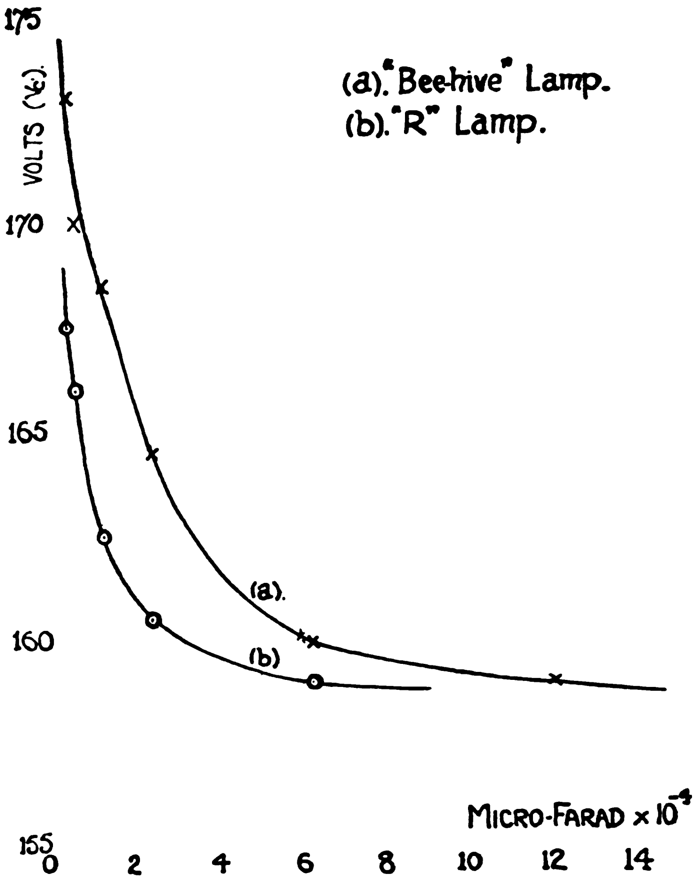
$$V_c' = 158{\cdot}2 + \frac{11{\cdot}3}{C}, \quad \ldots \ldots \quad (10)$$

and graph (*b*) more exactly by

$$V_c' = 158 + \frac{6{\cdot}0}{C}. \quad \ldots \ldots \quad (11)$$

It would appear, therefore, that the numerator of the second term of equation (5), which represents the quantity transference across the tube in establishing the glow discharge, is approximately constant, at least in the case of the smaller capacities. The first terms of equations (10) and (11) are of the value of the normal sparking potentials for the tubes.

Fig. 4.– Graphs showing the Relationship between the Capacity C and the least Voltage V_c' required to produce a Glow-Discharge.



It has not been possible so far to perform similar experiments on the air discharge-tubes, but it is hoped to be able to do so in the near future.

TABLE IV.

"R" lamp. RaBr ionizing agent.

$$V_c' = 158 + \frac{6}{C}.$$

C. in μF.	V_c'.	
0·00063	159	*159*
0·00025	160·5	*160·4*
0·000135	162·5	*162·5*
0·00007	166	*166·5*
0·00005	167·5	*170·0*

"Beehive" lamp. RaBr ionizing agent.

$$V_c' = 158{\cdot}2 + \frac{11{\cdot}3}{C}.$$

C. in μF.	V_c'.	
0·0012....................	159	*159·2*
0·00063	160	*160·1*
0·00025	164·5	*162·7*
0·000135.................	168·5	*166·4*
0·00007	170	*174·0*
0·00005	173	*180·6*

C. in 10^{-4} units. Italic figures give theoretical curve.

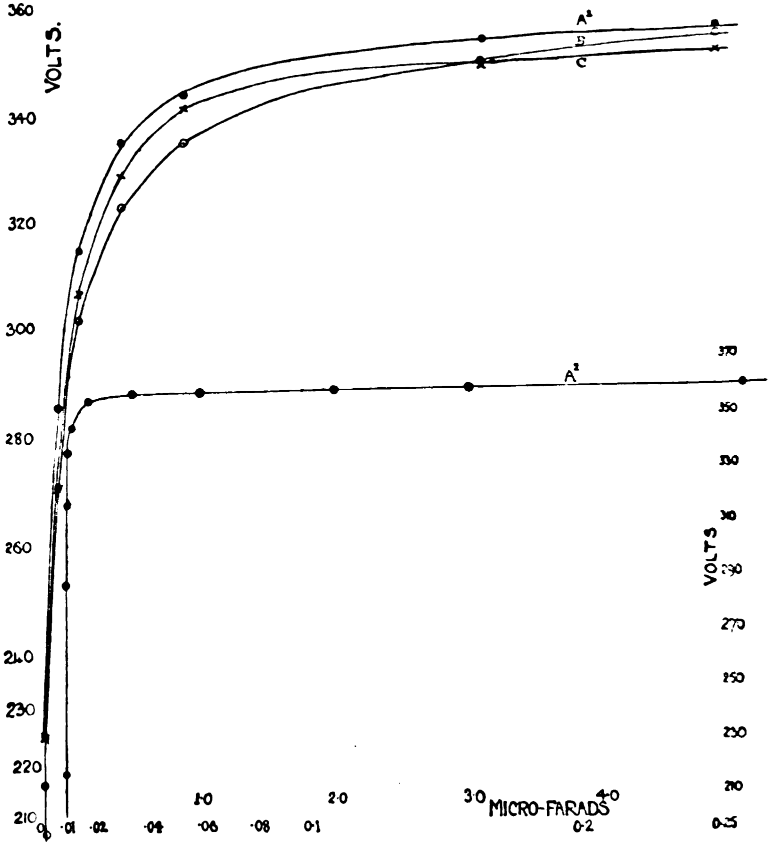
THE EXPERIMENTAL RESULTS FOR THE AIR DISCHARGE-TUBES.

The Variation of the Lower Critical Voltage with the Capacity for a Fixed Charging Voltage.

The variation of the lower critical voltage V_b' with the capacity for a fixed charging voltage was investigated in the case of the "Beehive" air discharge-tube at several different pressures. Fig. 5 shows the graphs of these relations, which are exactly similar to those obtained for the "Osglim" lamps (the actual values of the lower critical voltages are of course greater for the air discharge-tubes).

Owing to the lack of suitable capacities and batteries, it was not found possible to investigate the variation of V_b' with the charging voltage E over any great range of voltage, nor could it be determined whether there were minima for the V_b', C graphs like those obtained with the "Osglim" lamps.

Fig. 5.—Graphs showing the Relationship between the Lower Critical Voltage and the Capacity, for a Fixed Charging Voltage E.



"Beehive" type of air discharge-tube.
External ionizing agent, radium bromide.
Charging Voltage E, 580 volts throughout.

GRAPH A^2.—Large Capacities (From $5\mu F$ maximum). Pressure 0·75 mm. Hg. Graph is typical, similar curves being obtained for pressure range 3 mm. to 0·2 mm.

GRAPH A^1.—Large capacity scale (Maximum $0{\cdot}25\mu F$). Same results as graphed in A^2.

GRAPH B.—Similar to A^1, but pressure 2·92 mm.

GRAPH C. do. do. 1·67 mm.

TABLE V.

Air Discharge. "Beehive" lamp.

E = 580 volts. RaBr ionizing agent.

$p = (14·6 \times 0·02)$ cm. = 2·92 mm.

C =	5·0μF	4·0	3·0	2·0	1·0	0·5	0·25
V_b' =	365	365	365	365	361	358	355

C =	0·166μF	0·055	0·0315	0·016	0·0077	0·0022
V_b' =	350	335	323	302	271	208

E = 580 volts. RaBr ionizing agent. Air.

$p = (16·65 \times 0·01)$ cm. = 1·665 mm.

C =	5·0μF	4·0	3·0	2·0	1·0	0·5	0·25
V_b' =	362	362	359	356·5	356·5	356·5	352

C =	0·166	0·055	0·0315	0·016	0·0077	0·0022
V_b' =	349	341·5	329	307	271	225

E = 580 volts. RaBr ionizing agent.

$p = (7·45 \times 0·01)$ cm. = 0·745 mm.

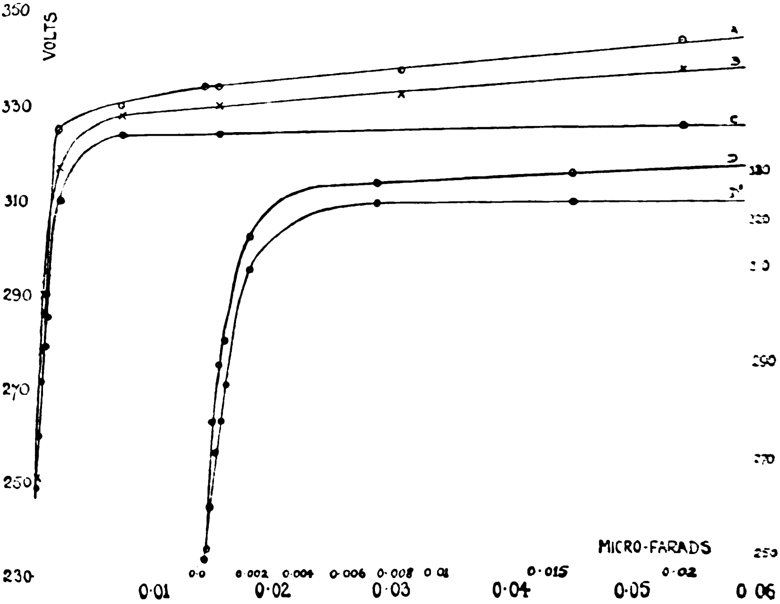
C =	5·0μF	3·0	2·0	1·0	0·5	0·25
V_b' =	360	358	357·5	357	356·5	356·5

C =	0·166μF	0·055	0·0315	0·016	0·0077	0·0022
V_b' =	354	344	335	315	286	216

Similar relations were found to hold for the molybdenum-wire electrode discharge-tube (see graphs of fig. 6). The conductivity of the tube is, however, much less than the conductivities of the other tubes, because the area of the cathode is very small. The capacity range of abnormal cathode fall extends consequently much further into the region of small capacities. Indeed, for capacities greater than some 0·2 microfarad, the actual time duration of the discharge becomes considerable and the conditions for accurate performance of the present method break down. (The time of "flash" becomes comparable with the time period of the ballistic galvanometer employed, and an initial "kick," always in the same direction, inhibits results (see Taylor and Stephenson, Journ. Scien. Instr. *loc. cit.*).)

It is observable that V_b' in the case of this tube diminishes slowly with the capacity down to about 0·004 microfarad, when rapid diminution with the capacity ensues. In previous experiments on the variation of the critical resistance for "flashing" (R_c) for this particular tube (see Taylor and Clarkson, Phil. Mag. *loc. cit.*) it was found that the critical resistance R_c decreased slowly and almost linearly with the capacity down to a capacity of 0·004 microfarad, when rapid diminution of R_c with further capacity reduction set in. The variation of the critical resistance is thus intimately connected with the variation of V_b'.

Fig. 6.—Graphs showing the Relationship between the Lower Critical Voltage and the Capacity, for a Fixed Value of the Charging Voltage E.



Air discharge-tube. Parallel molybdenum-wire electrodes tube.
External ionizing agent, radium bromide.
Charging Voltage E, 720 volts throughout.

Graph A.—Pressure 2·54 mm. Small capacity scale (maximum 0·055F).

Graph B.—Pressure 1·72 mm.

Graph C.—Pressure 1·13 mm.

Graph D.—Results for 1·72 mm. (graph B), but with enlarged capacity scale (0·02 μF.).

Graph D'.—Results for 1·13 mm. (graph C); enlarged capacity scale.

TABLE VI.

Molybdenum Wire Electrode—Air.

E = 720 volts.

Graph (A).

p.	C. in μF.	V_b'.
(12·7×0·02) cm. = 2·54 mm.	0·055	343
	0·0315	337
	0·016	334
	0·0147	334
	0·0077	330
	0·00223	325
	0·0012	290
	0·0010	286
	0·00063	286 (?)

Graphs (B) (& D).

p.	C. in μF.	V_b'.
(17·2×0·01) cm. = 1·72 mm.	0·055	337
	0·0315	332
	0·016	330
	0·0077	328
	0·00223	317
	0·0012	295
	0·00093	290
	0·00063	278
	0·00039	251

Graphs (C) (& D¹).

p.	C. in μF.	V_b'.
(11·3×0·01) cm. = 1·13 mm.	0·055	325
	0·016	324
	0·0077	324
	0·00223	310
	0·0012	285·5
	0·0010	278
	0·00075	271·5
	0·0005	260
	0·00028	249

We are indebted to Prof. G. W. Todd, of Armstrong College, under whose supervision the experiments were carried out, and to the Department of Scientific and Industrial Research for the grant which has enabled one of us to undertake the work.

CXI. *The Use of Commercial Plates in Research on the Latent Photographic Image. By* F. C. Toy, *D.Sc., F.Inst.P.* (*Communication No.* 44 *from the British Photographic Research Association Laboratories*)*.

THE fundamental importance of the photochemical law of the silver halide grain was recognized by Svedberg (*Zeitsch. wiss. Phot.* 1920, xx. p. 37) and Slade and Higson (Proc. Roy. Soc. 1920, 98 A, pp. 154–170) about the same time. Slade and Higson investigated the relation between the number of grains made developable, the time of exposure, and the intensity of the light. They used plates containing only a single layer of grains, so that these were all similarly situated as regards the incident light. Calling a the total number of grains present, and x the number made developable, they arrived at certain conclusions regarding the relation between

$$\log_e a/(a-x)$$

(which we will call n), the light intensity I, and the time of exposure t.

It is unnecessary to discuss their result in detail here; the main conclusion from their work was that the relation between n and I was expressed by an equation completely different *in type* from that which connected n and t. The results of much later work in the British Photographic Research Association laboratories has not confirmed this wide difference, and only partially confirmed the actual relationships which were found. Further, it has been found that a relationship which holds for one emulsion is not necessarily exactly the same for another, and this is the main difficulty in the way of establishing exact quantitative relations between the photographic effect and the conditions of exposure.

Since Slade and Higson's paper was written, it has been realised that the quantity we have called n is of great significance, in that it is actually the numerical measure of the number of reduction centres (expressed as average number per grain) which are formed by the light. This has led to many laborious experiments on the relation between n and the exposure, and for many emulsions it has now been shown that the curve connecting n and E ($E = I \times t$, where I or t is variable), for monochromatic light and normal exposures, is similar to those shown in fig. 1. There is a distinct "period of induction" followed by a rapid increase of dn/dE from zero to a constant value when the straight line portion is reached. The top of the curve need not be considered here, since the greater part of the photographic effect is produced while n is still on the straight line portion. It has been shown that the curved foot to the straight line is short compared with the range over which the straight line itself extends, and the object of this paper is not affected if we make the approximation that the straight line continues down to the exposure axis, cutting this at a value of the exposure which may be called the inertia value (e). If α be the angle the straight line makes with the E axis, the equation connecting n and E may be written

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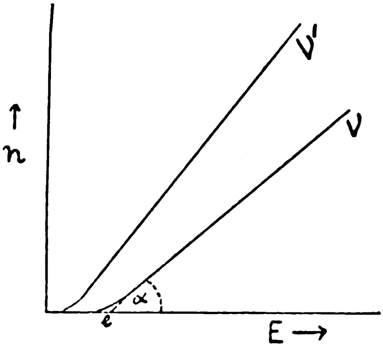
* Communicated by Dr. T. Slater Price, O.B.E., D.Sc., F.R.S.

Fig. 1.



$$n = \phi(E - e)$$

where $\phi = \tan\alpha$, and e = inertia value of exposure.

Taking this equation as the starting point, consider the general case of two monochromatic lights of frequency ν and ν'. Let these frequencies be such that the light absorption by the silver bromide grain is very much greater for ν' than for ν. This means that for equal incident energy of each light, more photographic effect is produced by ν' than by ν (Phil. Mag. xlviii. pp. 947–961 (1924)) and the curves for the two lights will be as shown in fig. 1.

The equations for these will be

$$n = \phi(E - e),$$
$$n = \phi'(E - e'),$$

where $e > e'$ and $\phi' > \phi$.

Now apply this result to a consideration of the effect produced in a *thick layer* of emulsion as it occurs on ordinary commercial plates. We will consider the emulsion divided into a large number of layers, each so thin that it may be considered to behave very nearly like a single layer. As the light penetrates the film, the intensity will decrease, the rate of decrease being much greater for ν' than for ν, since the silver bromide absorbs the former much more strongly (according to our assumption).

Let p and q be the ratios of the intensity transmitted to that incident upon any layer, for the lights ν and ν', respectively, that is, p and q are the transmission factors of a layer. We will assume p and q are constant throughout the thickness of the emulsion *.

If the incident intensity is I, then, for ν, the intensities incident on successive layers will be

$$\mathrm{I},\ p\mathrm{I},\ p^2\mathrm{I},\ \ldots\ldots$$

and for ν'

$$\mathrm{I},\ q\mathrm{I},\ q^2\mathrm{I},\ \ldots\ldots$$

Let the plate be given an exposure $\mathrm{E}\ (=\mathrm{I}\times t)$. Then applying the law for the single layer to each layer in succession the total number of centres (N) formed will be, by the light of frequency ν,

$$\mathrm{N}=n_1+n_2+n_3+\ldots\ldots=\phi(\mathrm{E}-e)+\phi(p\mathrm{E}-e)$$
$$+\phi(p^2\mathrm{E}-e)+\ldots\ldots \quad . \quad . \quad . \quad (1)$$

and by the light ν'

$$\mathrm{N}'=n_1'+n_2'+n_3'+\ldots\ldots=\phi'(\mathrm{E}-e')+\phi'(q\mathrm{E}-e')$$
$$+\phi'(q^2\mathrm{E}-e')+\ldots\ldots \quad . \quad . \quad . \quad (2)$$

The first term in each of these expressions gives the number of centres formed in the top layer only. If the exposure is very small, so that E is just greater than e, but $p\text{E}<e$ and $q\text{E}<e'$, then all the terms except the first are negative, implying physically no photographic effect in either case except in the first layer. With all exposures less than this value, the ratio of the numbers of centres produced by the two lights is given by

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* Abney showed (Camera Club J. p. 173, 1899) that the effective opacity of each layer is *lower* than that of the one above it in the series. Bloch and Renwick confirmed this (Phot. J. lvi. pp. 49-66, 1916) and came to the conclusion that the correct relation between the density (D) and the weight of silver bromide per unit area (W) of plate, was expressed by an equation of the type $\mathrm{D}=a\mathrm{W}^b$, where a and b are constant, b being <1. If the absorption for each layer of silver bromide were the same, b should be 1, instead of less as proved by Bloch and Renwick. They only determined the values of b in one case using monochromatic light and found it to be 0·82. The approximation made in the paper does not, however, affect the general result, which depends essentially on the fact that the terms in q (equation 2) decrease much more rapidly than the corresponding terms in p (equation 1).

$$\text{N}'/\text{N}=\frac{\phi'}{\phi}\times\frac{(\text{E}-e')}{(\text{E}-e)}$$

which becomes infinite when $\text{E}=e$. This is, of course, expressed by curves in fig. 1. As the exposure is increased the light penetrates deeper into the film, and centres are formed in other layers than the first; that is, other terms than the first contribute their share to the total effect produced. The value of the successive terms added will depend on the values of p and q. In the case we have taken, the light of frequency ν' is much more strongly absorbed than ν, so that the transmission factor q is much less than p. Each of these being a fraction less than 1, the terms in q will decrease much more rapidly than the corresponding terms in p. At a certain term, say the $(r+1)$th, $q^r\text{E}$ is less than e', while $p^r\text{E}$ may still be considerably more than e, that is, more terms of equation 1 than 2 must be taken to get the total effect due to the incident intensity. In fact, as the exposure is increased and the light produces effects deeper down in the emulsion, N may become greater than N$'$, that is, *the relative effects produced in a layer of emulsion may be completely reversed if the thickness of the layer is varied.*

The usual and simplest effect to observe in a single-layer plate is the percentage of grains which are made developable, and this is easily obtained if the number of centres produced is known (Phil. Mag. xliv. pp. 352–371 (1922)). If x is this percentage, the values of the percentages for the different layers are given by

$$\left.\begin{aligned}x_1&=100(1-e^{-n_1})\\ x_2&=100(1-e^{-n_2})\\ &\cdots\cdots\end{aligned}\right\}, \quad \ldots\ldots \quad (3)$$

where n_1 and n_2, etc., are the average number of centres per grain in a single layer, and x_1, x_2, etc., the corresponding percentages changed. To obtain the percentage of grains changed in each layer of the emulsion, each term in n in equations 1 and 2 must be converted separately to the corresponding x term by means of equation 3.

If we consider that we are examining an area of plate such that there are 100 grains in each layer, the addition of the terms in x will give us relative values of the total number of developed grains in all layers. If we call X and X′ the total number of developable grains throughout the whole thickness of emulsion for ν and ν' respectively, we get finally from 1, 2, and 3

$$\mathrm{X}=x_1+x_2+x_3+\ldots.=100\{(1-e^{-\phi(\mathrm{E}-e)})$$
$$+(1-e^{-\phi(p\mathrm{E}-e)})+(1-e^{-\phi(p^2\mathrm{E}-e)})+\ldots.\}. \quad (4)$$
$$\mathrm{X}'=x'+x_2'+x_3'+\ldots.=100\{(1-e^{-\phi'(\mathrm{E}-e')})$$
$$+(1-e^{-\phi'(q\mathrm{E}-e')})+(1-e^{-\phi'(q^2\mathrm{E}-e')})+\ldots.\}. \quad (5)$$

As an example, let us take a case which has been investigated in our laboratory, viz., that of the effects produced by the blue line ($\lambda=4358$ A) and the ultra-violet line ($\lambda=3650$ A) of the mercury arc. The following values of the factors given in equations (1) and (2) are of the order of those actually found for the two frequencies mentioned, in the case of a pure bromide emulsion with small even grains:

$$\phi=0\ 5,\ \phi'=2{\cdot}0\ ;\quad e=0{\cdot}5,\ e'=0{\cdot}1\ ;\quad p=0{\cdot}8,\ q=0{\cdot}5.$$

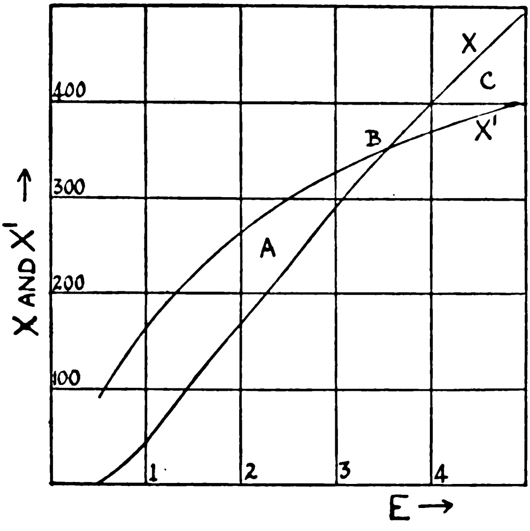
The value of the exposure is given in units of $1{\cdot}2\times10^{-6}$ calories per sq. cm. Using these data, it is easy to calculate the values of X and X′ from equations (4) and (5) for the various values of E. These are given in the table and plotted in fig. 2.

It will be seen at once, that for a thick layer of emulsion the relative effects produced by ν and ν' will depend on the exposure; thus if $\mathrm{E}=0{\cdot}5$, $\mathrm{X}'/\mathrm{X}=\infty$ and this gradually decreases with increasing exposure until $\mathrm{X}'=\mathrm{X}$ when $\mathrm{E}=3{\cdot}5$. For bigger values of E, X becomes greater than X′.

	Total grains changed in all layers.	
E.	X.	X′.
0·5	0	88
1·0	43	169
2·0	172	267
3·0	293	335
4·0	398	364
5·0	492	399

This point has been tested experimentally using the same frequencies as above, and thick plates of the same emulsion as gave the curves in fig. 1. Two strips of the same plate were exposed behind a wedge to known intensities of the blue and ultra-violet, the gradation of the wedge for each light being known. From this it is easy to calculate the intensities on the plate at every point, and the density after development of these points can be easily measured. Now we know that, at any rate approximately, the density of a developed silver image is proportional to the quantity of silver present, that is, to the total number of developed silver grains (assuming uniformity of grain size), so that if we plot density against intensity for each light we should

Fig. 2.



get curves similar to those obtained theoretically in fig. 2. That this is so is seen very clearly from fig. 3 and fig. 4, which give similar curves, one being obtained by varying the time and keeping the intensity constant, and the other by varying the intensity.

It should be pointed out that this kind of result would not necessarily be observed with *any* different monochromatic lights since it depends essentially on the great difference between p and q, which in turn depend on the great variation, with frequency, in the light absorption by the silver bromide. If the frequencies used were in a range of the spectrum over which the silver bromide absorption was constant, the curves shown in figs. 3 and 4 would not be obtained, and the light which gave the greater effect on a single-layer plate would also give the greater effect on a thick layer, whatever the exposure.

Fig. 3.

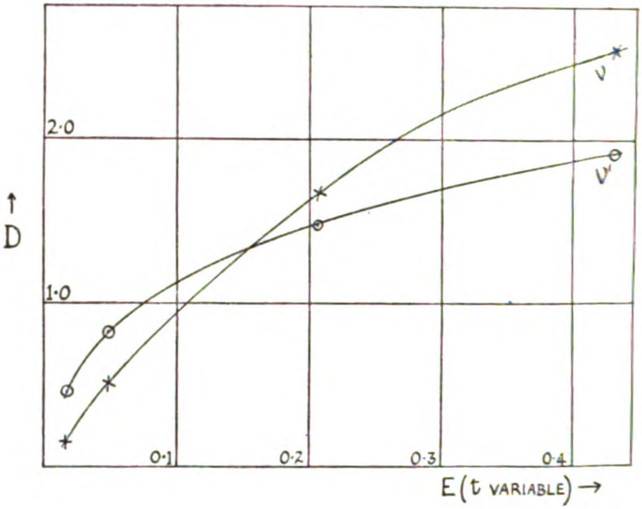
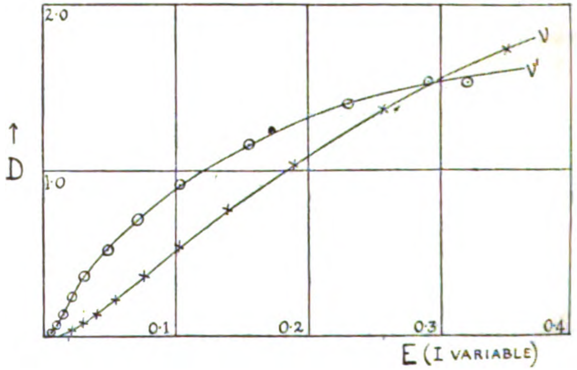


Fig. 4.



It follows that it may be exceedingly dangerous to use ordinary thickly coated commercial plates for experiments on the quantity of energy of different frequencies necessary for the formation of the latent image. This, however, has recently been done by Helmick (J. Opt. Soc. Amer. ix. pp. 521–540 (1924)). Using four radiations of wave-lengths 3650, 3131, 2653, 2537 Å., Helmick investigated the relation between the total energy incident and the total number of developable grains produced *throughout the whole thickness of the emulsion coating.* Knowing these, he has calculated the average number of quanta per grain which are required to make one grain developable. He found that, on the average, the number of quanta required for this purpose decreased as the frequency of the light decreased, and drew the conclusion that the efficiency of light quanta in producing developable grains increases as the frequency decreases.

Now, as far as is known, the variation of the light absorption by silver bromide with frequency has never been investigated over the range of frequencies used by Helmick, so that it may either be constant or it may vary enormously as we know it does in the visible and near ultra-violet. Slade and Toy (Proc. Roy. Soc. 97 A, pp. 181–190 (1920)) have shown that it is increasing very rapidly with increase of frequency from the visible down to about 3400 Å, the limit of their investigation.

The point is that Helmick's result is meaningless without a knowledge of the silver bromide absorption curve in the region employed by him. For, if this absorption does vary very rapidly with frequency in that region, and if, for the emulsion he used, the same relation holds between n and E as holds for the emulsion used here (as it probably does) the blackening curves for the different lights would be similar to those we have obtained here (though they would be reversed in order if the absorption were decreasing with increase of ν instead of increasing), with the result that *the conclusions drawn as to the relative efficiency of different frequency quanta would depend on the purely arbitrary exposure given to the plate.* Thus, if Helmick's exposures were such as to be in the region of A in fig. 2, he would have found that more grains were made developable by the light of greater frequency, and would have concluded that the efficiency of quanta as regards the formation of developable grains increased with the frequency. If he had given to his plate exposures corresponding to the region marked B in fig. 5 he might have concluded that the quanta of different frequencies were equally efficient, while at an exposure such as C the order of efficiency would have been completely reversed.

All this points to the necessity for using single-layer plates for all accurate work on the relation between the energy required for the formation of the latent image and the frequency. Under such conditions there is as yet no evidence sufficiently definite for us to draw any other conclusion than that, per quantum absorbed, all frequencies of ultra-violet light are equally efficient in making developable the silver halide grain.

In conclusion, the author wishes to express his thanks to Dr. Slater Price for the interest which he has shown in this work.

CXII. *The Combustion of Carbon-Monoxide Mixtures.* By J. H. Crowe, *M.Sc.*, *and* A. H. Newey, *M.Sc.*, *Bowen Research Scholar* *.

It has long been recognized that the Air standard cycle, as representing the ideal efficiency for an Internal Combustion Engine, is only permissible because of the lack of precise knowledge concerning the physico-chemical phenomena taking place during combustion. The Air standard postulates an "ideal air" with constant specific heat, and assumes that, in a mixture of this air and combustible gas, heat is added instantaneously, and, further, that during combustion there is no dissociation of the products.

The present investigations, which are part of a series undertaken at the Birmingham University, are an attempt to determine something of the manner in which combustion proceeds when a mixture is exploded in a closed vessel, more particularly to measure the velocity of propagation of the flame front. The apparatus necessary has been rather considerable, and this was designed and constructed by by J. L. Pearson and R. C. A. Anderson. To the former is due the credit of developing the method of attacking the problem.

In order to simplify the conditions and eliminate wall action, the explosion vessel is a sphere of 16 inches diameter, and ignition is effected at the centre. The original method suggested for recording the passage of the flame was first put forward by J. D. Morgan ('Engineering,' October 1919). This consisted of having an insulated gap formed by two steel electrodes in the path of the flame, and in series with this a second gap for recording purposes and a condenser of suitable value. When the first gap is bridged by the flame, the condenser is discharged and the spark at the other gap can be recorded photographically.

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* Communicated by Prof. F. W. Burstall, M.A., M.Sc.

This arrangement will work very well when a bunsen flame is flicked through the gap, but when tried in the sphere it failed completely. After much experimental work the present method was developed, and this is essentially as follows.

The condenser is replaced by a motor alternator, the voltage of which is transformed up to about 8000. One side of the transformer is earthed, and the other side is connected through a variable liquid resistance to the external adjustable gap. Connexion is made from this to the central electrode of a large specially designed sparking-plug, which is screwed to the sphere. The sphere, and therefore the plug, is earthed. The cable connecting the two gaps has a certain capacity to earth, and, if the external gap is closed down slowly when the high voltage is on, a charging current can be made to flow and give a continuous discharge through the gap, while the gap in the sphere is in no way affected. When the flame reaches the points of the plug an arc is struck at both gaps, and the change from the capacity spark to the arc is plainly photographed on a falling plate. A more detailed description of some of the components of the apparatus can now be given.

The sphere is a mild steel forging, 16 inches in internal diameter, with walls 1½ inches thick, and was machined from the solid. The two halves are bolted together by 18 1½-inch nickel steel bolts. There are 24 plug-holes disposed along different radial lines, although only 17 plugs, including the firing plug, are used. In each hemisphere there are two inlet passages. One valve opens to a mercury U-tube and vacuum-pump, one is connected to the compressed-air bottle, another controls the gas (and oxygen when used), and the fourth one opens to the atmosphere and is also used for passing hot air through the sphere after an explosion. The inside surface of the sphere is silver-plated, as it had been found that, when using coal-gas, considerable corrosion took place, owing to the deposition of moisture.

The internal gaps which project into the sphere are arranged by screwing steel electrodes of varying lengths into the base and central spindle of large sparking-plugs, which were specially made by Messrs. Lodge Plugs Ltd. The electrodes and bases of the plugs are silver-plated. The gap at the points is normally 5 mm., but this is raised somewhat depending on the initial pressure used. The plug having its points at the centre of the sphere is used as the ignition-plug and has a much smaller gap. Ignition is effected by means of a 6-volt accumulator and 6-inch trembler induction-coil. In order to time the firing of the charge at the right moment, an extra switch in the primary of the coil is arranged—a wiper switch on the plunger of the falling-plate camera.

There are five external gaps, and these are contained in a light-tight box, with a lens behind each to focus the capacity spark or arc on to the falling plate. The electrodes of each gap are carried in a frame of ebonite, the top one being fixed into an ebonite screw to give vertical adjustment. Focussing adjustment is also provided. Only three of the gaps are used, one being in series with the particular plug required and another in series with the firing plug, so that the ignition-spark is also recorded on the plate. The purpose of the third gap will be explained later.

The falling-plate camera is the standard camera made by The Cambridge Scientific Instrument Co. Ltd. The plate is released by an electro-magnetic catch and falls at a uniform speed controlled by a plunger working in an oil cylinder. The camera-box makes a light-tight joint with the external gap-box.

The time is put on to the plate by means of a vibrating bar time-marker, also a standard instrument. The bar is vibrated electrically, and drives a small synchronous motor having a spoked disk on the end of the armature. Light from an arc lamp passes through an aperture on to the falling plate, and the light is cut off regularly by the spokes, giving a line on the plate broken in hundredths of a second.

Besides measuring the flame velocity, a pressure record is taken on the same plate. For this purpose a Burstall Optical Indicator is fitted (for description see Proc. Inst. of Mech. Eng. 1923). The piston has been replaced by a diaphragm. This has two corrugations in it and is cut out of the solid, so that it is perfectly encastre, thus reducing any hysteresis effect.

In order to save time in the experimental work, a fan is used to stir up the mixture before firing. The fan spindle passes through the body of a plug screwed into the sphere and is driven at 800 r.p.m. by a small motor. The initial pressure is taken by a packing of lead shavings, and the explosion pressure by screwing back the spindle on to a seating on the plug after the fan has been stopped. The fan-blades, which are silver, are hinged on to the boss in order to pass the 1¼-inch hole, and when in action are close to the inner wall, so as not to affect the progress of the flame. The remaining exposed parts are all silver-plated.

An electric heater also screws into the sphere. This helps to drive off any moisture that may be deposited, and also to adjust the initial temperature if required.

The only combustible gas that has been used is carbon monoxide, and a small plant was put down for its manufacture. The gas is prepared by the usual laboratory method, the action of concentrated sulphuric acid on formic acid, the temperature being about 100° C. The gas is collected in a 6 cu. ft. holder and from there drawn off by a portable two-stage compressor into a storage-bottle. An oil separator is interposed between the compressor and the bottle, the gas passing up through a spiral of wire and any oil that has been sent over is deposited and run off. As used, the gas is saturated and the air is in the normal hygrometric state as it would be in gas-engine practice. The purity of the gas is 97·5 per cent., the remainder being air.

In order to obtain a complete record of the flame, twelve explosions for any set of conditions are necessary (only twelve plugs are available). After each explosion the sphere is exhausted and hot air passed through. After a second exhaustion, the air and gas are admitted very slowly in the correct proportions. The U-tube is used for pressure up to three atmospheres, and above this a Bourdon gauge. The mixture is then stirred for 20 minutes, which was found to give complete diffusion, and then left for a few minutes for eddies to die down. After the time-marker and indicator have been put on, the high voltage is switched on and the external gaps adjusted to give a continuous spark discharge. The mixture is then exploded by dropping the plate.

A vast number of difficulties with the apparatus presented themselves at first, but these have gradually been eliminated until experiments can now be carried out fairly continuously, although by no means rapidly. A considerable number of results were discarded before those given here were obtained. These can be repeated and the same results obtained within the limits of the small errors introduced in the proportions of gas to air, etc.

In the course of the preliminary experiments some information was obtained of the effect of diffusion on the manner of the flame spread. In one experiment the fan was only left on for five minutes. It was afterwards found that 20 minutes is necessary to obtain diffusion sufficiently

TABLE I.

Initial Pressure, 2 atmospheres absolute.
Initial Temperature, 17° C.

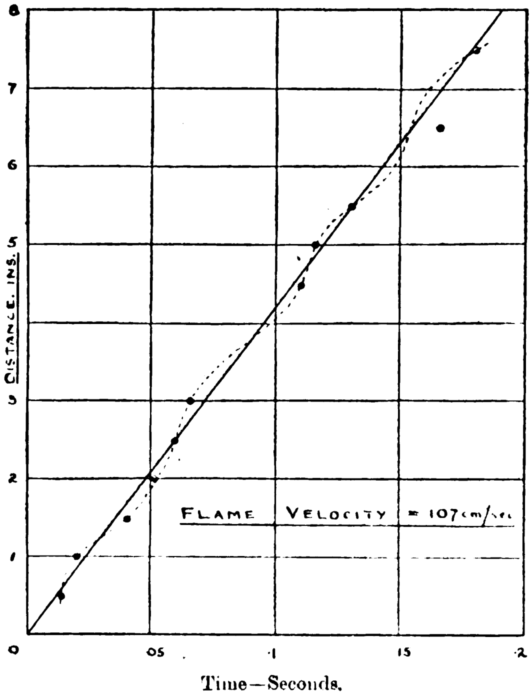
Per cent. Gas (97·5 per cent. pure).	Flame Velocity. cm./sec.	Max. Press. Time. secs.	Max. Pressure. lb., sq. in. abs.	Pressure Ratio.
17	26·6	...	...	...
20	50·7	·80	169·5	5·77
25	84·1	·385	209	7·12
30	107	·231	231·5	7·86
35	139	·211	240	8·16
40	145	·175	243	8·27
45	137	·170	242·5	8·25
50	129	·189	224·5	7·65
55	101	·251	208·5	7·10
60	77·5	·390	178	6·05
65	...	·920	143	4·87

complete to give consistent results. Plotted out as Time-distance ordinates for each plug the points were rather erratic, and on repetition were not constant. By repeating each point two or three times, and carrying out two such experiments, one at one atmosphere initial, another at two, some idea of the manner in which the flame spread could be obtained. There appear to be four main effects resulting from incomplete diffusion: (1) The Velocity varies along different radial lines; (2) There is an accelerated motion after about one-half of the distance is travelled; (3) The mean velocity is lower than for complete diffusion; (4) The time of combustion is increased. With the exception of (2) these might have been predicted beforehand. It would seem that the acceleration must be due to the increase of homogeneity resulting from the adiabatic compression of the unburnt portion of the mixture. The decrease in the mean velocity is quite considerable. For a 25 per cent. gas mixture, the mean flame velocity was 48·9 cm./sec. When completely diffused the constant velocity is 97·7 cm./sec. The corresponding times of combustion—*i. e.*, the times to attain the maximum pressure—are ·416 sec. and ·280 sec.

Fig. 1 gives a velocity curve which is typical of all the curves obtained for any Air/Gas ratio and any initial pressure, and in which diffusion is complete. A mean straight line can be put through the points. This uniform velocity is one of the chief results that these investigations have yielded. It has usually been assumed that when a mixture is exploded in a closed vessel there will be an accelerated motion. Several reasons have been advanced in support of this:—(1) The rise in temperature produced by the combustion of the portion first inflamed will cause an expansion, and this will have the effect of projecting the flame front forward at an increasing velocity. (2) As the flame advances the unburnt portion is compressed, thus bringing it nearer the ignition temperature. Less heat will therefore be required from the burning zone to influence it. (3) The increase of pressure, quite apart from the rise in temperature, will increase the speed of combustion. (4) Also, if we look on flame-propagation from a point of view of conduction of heat, there will be an increase in the temperature difference between burning and unburnt zones due to the compression of the total change.

Fig. 1.

Mixture—30 per cent. Gas, 70 per cent. Air.
Initial Pressure—2 Atmos.



It is now known that (3) is not an accelerating but a decelerating influence in the case of carbon monoxide and air. This will be referred to later.

It has yet to be shown that flame spreads with a constant velocity in any other than carbon monoxide mixtures. In the case of hydrogen, Nagel has shown that an increase of initial pressure results in a lower time of combustion, and therefore presumably in a higher flame velocity. The flame speed in hydrogen therefore might possibly be accelerated. The difference in the detonating properties of these two gases is also well known, and it would seem quite likely that this depends to a large extent on the possibility of an accelerated flame motion and therefore of the behaviour of the gases when exploded under different pressures. No experiments have been done on hydrogen as yet, and it is rather doubtful if records will be obtained with the present apparatus. The slower combustion of carbon monoxide at higher pressures is the only fact that will explain a constant velocity, and it must be inferred that, since all the forces operating are interdependent—that is, they all depend on changes of pressure,—they can only be developed to such an extent that they will always counterbalance.

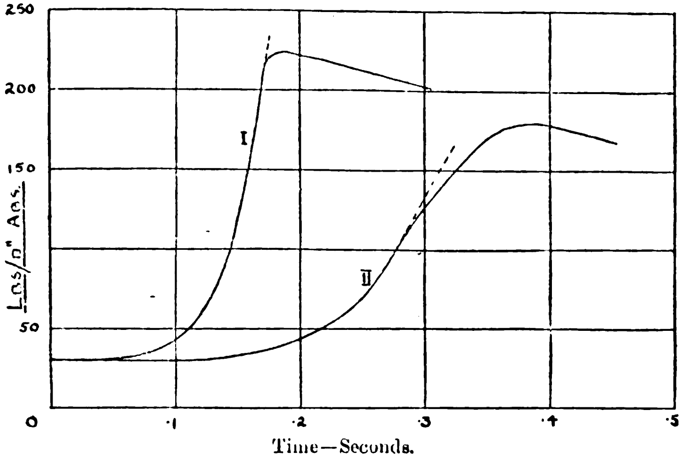
It will be seen from fig. 1 that a wavy line can be put through the actual points. This is not due to experimental errors, as these are much smaller than the observed discrepancies. It was thought at first that the plugs might be so disposed that the effects of convection would produce these differences from the mean velocity. Some experiments were done to find out how the flame front is distorted by convection currents, and from these it is fairly certain that in the upper hemisphere the flame front is truly spherical. Below the centre line there is a flattening out of the flame even at velocities of over 100 cm./sec. Most of the plugs are in the upper half, and only one plug in the lower half would show this lag. There is little doubt now that the wave is a true oscillation of the flame front. This oscillation is always present with any mixture and any initial pressure, the frequency being fairly constant and the amplitude, except when much higher temperatures are recorded, is also constant.

If resonance of the whole mass is set up, analogous to that found in tube experiments, the frequency of the vibrations would be higher (Mason & Wheeler, Chem. Soc. Trans. 1919). The initial oscillation must be started by the pressure waves that are being sent out both through the burning core and to the walls. Those will be reflected and cross and re-cross at the flame front. The speed of those through the burning mass will be much higher than those through the unburnt part, and it may be assumed that the actual frequency of the flame is the resultant of these two vibrations.

An interesting point about all the pressure records obtained, two of which are reproduced in fig. 2, is that the flame velocity may be obtained approximately from them. With carbon monoxide-air mixtures, in no case is the combustion of the whole mass complete when the flame has reached the walls. During the subsequent combustion cooling is taking place, and the time when this begins is shown by a point of inflexion on the pressure curve. This has been used later in an estimation of cooling losses.

Fig. 2.

Pressure Records— I. 50 per cent. Gas, 50 per cent. Air.
II. 60 per cent. Gas, 40 per cent. Air.

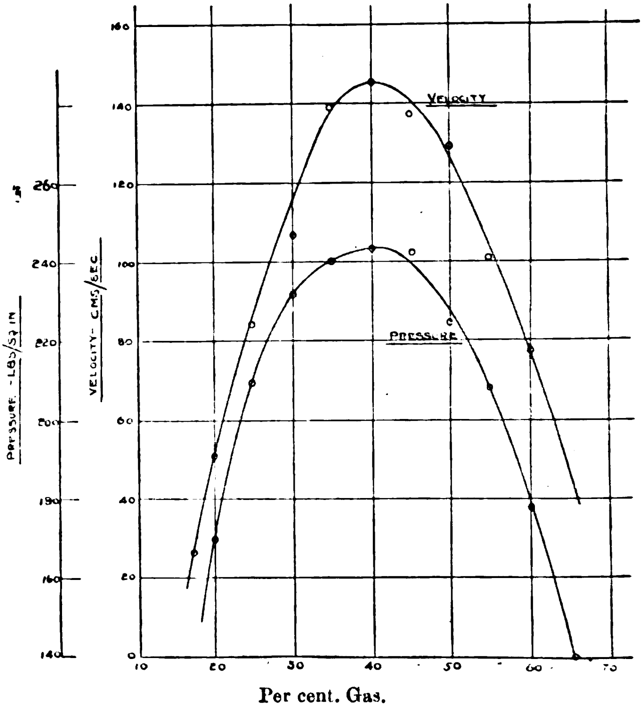


In Table I. are given the results of a series of experiments with different mixture strengths. The flame velocity and maximum pressure are plotted in fig. 3. The peaks of both curves occur at about 40 per cent., the theoretical mixture is 30 per cent. As far as the velocity is concerned, this is in agreement with practically all determinations of flame-propagation, whatever the conditions. Unfortunately, very few experiments have been done on propagation in a tube with carbon monoxide. With methane and hydrogen the shift of the peak of the curve from the theoretical mixture might be explained simply by a theory of conductivity, the thermal conductivity of both of these gases being greater than air.

The conductivity of carbon monoxide, however, is about the same as that of air.

Considering the pressure curve, Tizard and Pye (Proc. Auto. Eng. 1920) have shown that the phenomenon of the maximum pressure occurring with a rich mixture may be accounted for by the dissociation of the products of combustion. This occurs because the percentage of excess carbon monoxide is increasing, and this has a powerful effect in limiting the amount of dissociation that can occur.

Fig. 3.



It would seem at the outset, then, that the velocity of the flame is mainly a function of flame temperature, and that the position of the peak of this curve is also determined by the amount of dissociation.

If we accept some theory of conduction, then flame speed will depend on the ignition temperature of the mixture as well as on flame temperature and conductivity. This ignition temperature, however, probably plays a very small part indeed, if any, in determining the velocity of flame-propagation. In some later experiments where the rise of temperature, due to adiabatic compression, of the unburnt mixture is much higher, because there is less subsequent combustion, there is still no sign of an accelerated motion which might be expected if flame velocity were determined by the rate at which one layer immediately in front of the flame can be raised to the ignition temperature.

It is difficult also to explain how a detonation wave can travel through a mixture which has not been previously compressed up to the ignition temperature, as it does in an open-ended tube. Any conduction theory of propagation appears therefore to be quite untenable.

There is a distinction between the rate of combustion and the rate of propagation of combustion, although the two must be closely related, and at the flame front itself precisely the same process must be going on that is going on in the flame zone. If, then, we neglect altogether the time required to raise a layer up to the ignition temperature, we should expect that the velocity of the flame would be determined by the same factors that determine the rate of combustion—that is, flame temperature and the mass factor. If this is so,

$$V = KC_1^2C_2,$$

where $\log K = A + BT$ (Nernst) and C_1, C_2 are the concentrations of carbon monoxide and oxygen.

As the peaks of the two curves of pressure (and therefore temperature) and velocity are practically at the same mixture, the value of the K would be such that the temperature factor overwhelms the mass factor. The latter alone would give a maximum at 66 per cent. This does, however, operate in the right direction, as is seen if we take a horizontal line on the Velocity Curve. For the same flame velocity the temperature of the stronger mixture is lower than that of the weaker.

In the preliminary experiments attempts were made to obtain more than one velocity determination for each explosion by using two recording plugs at different distances from the centre, each in series with its own external gap. By suitable adjustment of the electrical conditions two records could be obtained with fair regularity, but on examination it was found that the second record did not give the velocity but the arc struck invariably some time after the flame had passed through the plug-points. In addition, there was no consistent time-lag. On examining a number of records it was found that the first plug determined the striking of the arc at the second—that is, the first arc ceased and the second commenced at a constant time from striking for a particular first plug, irrespective of the particular second plug used. It was thought that when a certain phase in the combustion was reached at the first gap, the tendency to arc at the second overcame the effect at the first. This was tried outside the sphere, using two plugs and two bunsen flames, but in most cases it gave the condition for the velocity at the second plug. It had previously been found that no reliance could be placed on bunsen experiments outside the sphere. The conditions are very different. Since, however, the presence of the second plug did not affect the velocity determination at the first, two plugs were used throughout the greater part of the experimental work.

All results using any mixtures of CO and air gave similar results, and on analysis it was found that the particular phase of combustion recorded at the wall of the sphere occurred in most cases just after the attainment of maximum pressure. That is to say, the records indicate the approach to complete combustion when there is a great diminution of chemical activity. It is realised that complete combustion can only be approached asymptotically, and, in fact, using large resistances in series, arcs have been produced which show this tailing off effect.

That combustion is certainly taking place after the flame reaches the wall is shown by the pressure results—that is, the rise in pressure beyond the point of inflexion. Hopkinson (Proc. Roy. Soc. 1906), using coal gas, observed that the flame filled the vessel before maximum pressure. Wheeler (Trans. Chem. Soc. 1918), using methane, found that the flame filled the vessel at the time of maximum pressure, but his pressure records are not above criticism. Hopkinson explains his subsequent pressure rise by the fact that a hot core is produced at first which must equalise through the vessel, the change in specific heats giving the additional pressure rise. If this is the case in some of the present faster-burning mixtures which approach Hopkinson's velocities, there should be less rise in the slower burning mixture owing to greater time available for temperature equalisation. The reverse is invariably the case, and the only possible explanation is prolonged combustion. From this can be generalised that combustion does not take place instantaneously at any spherical shell using carbon monoxide and air, and probably does not do so with any other gas, although in some cases it approaches instantaneous combustion—*e. g.*, hydrogen and oxygen.

In all mixtures of CO and air, it was found that combustion was nearing equilibrium at the centre as the flame strikes the wall. This, of course, probably only holds for this size of sphere. A curve can be plotted showing the time of combustion at any spherical shell against the radius of the shell. A parabolic curve is produced, giving a maximum time for most mixtures at a radius of 2½ inches, minimum at the wall, excluding of course a very thin layer in contact with the cold wall, and at the centre a time midway between the maximum and minimum.

By assuming a uniform rate of heat addition in any spherical shell, together with the time of combustion and the flame velocity, the proportion of total heat evolved can be calculated for any instant after sparking the mixture. A simple integration gives the proportion of heat addition for the whole sphere. Assuming constant specific heat, the rise in pressure is proportional to the actual heat evolved. Plotting heat evolved against time, it was found that the theoretical heat evolved was considerably less than the actual. With variable specific heats, the actual heat curve should be higher still. This indicates that heat addition in a spherical shell takes place more rapidly at first and then at an ever-diminishing rate. Presuming combustion to follow the law of mass action, the mass factor rapidly counteracts the temperature coefficient, giving an asymptotic approach to chemical equilibrium.

In making temperature calculations for gaseous explosions, certain assumptions have to be made and certain data used. The principal assumption made in these calculations is that chemical equilibrium is nearly reached at the time of maximum pressure, and the only "after-burning" that takes place is the recombination of dissociated products. In all cases the peak of the curve is reached when the rate of heat addition equals the rate of cooling. From the slopes of the pressure curve just before and after the peak there must be a very sudden change, which cannot be satisfactorily explained by the "after-burning" theory. This, however, would be the result expected if chemical equilibrium were reached.

At these high temperatures very little reliable information is available for volumetric heats and equilibrium constants for dissociation. On examination of the existing data, the following results of Pier and Bjerrum have been thought most reliable :—

Vol. ht. Nitrogen.. $4{\cdot}9+{\cdot}45\times10^{-3}t$.
Carbon Dioxide .. $6{\cdot}8+3{\cdot}3\times10^{-3}t-{\cdot}95\times10^{-6}t^2+{\cdot}1\times10^{-9}t^3$

being the mean vol. hts. between 18° C. and t° C.

For the equilibrium constants for CO_2 $K=\dfrac{P^2_{co}\times P_{o_2}}{P^2_{co_2}}$

$$2000\text{–}2500 \text{ abs.} \quad \log K=9{\cdot}41-\frac{29500}{T\ (\text{abs.})}$$

$$2500\text{–}3000 \text{ abs.} \quad \log K=9{\cdot}57-\frac{29920}{T}$$

For the calculation of the mean temperature from the pressure, a knowledge of the contraction factor is necessary. This depends upon the degree of dissociation, which in turn depends upon temperature and pressure. In the experimental work, from different explosions of similar mixtures under similar conditions, slightly varying maximum pressures were obtained. The variation in maximum pressure was sometimes as much as 2 per cent. from the mean value, with the variation of time to reach maximum pressure somewhat greater. These discrepancies cannot be wholly explained by variations in mixture strength, as great care was taken over this to ensure results being as uniform as possible. Similar phenomena were observed by Bjerrum (*Zeit. Phys. Chem.* 1912) in his CO experiments, but with no other gases. Mean values have always been taken and results for different mixtures plotted, and the values used in the calculations taken from the mean curve. This method was adopted for all experimental results, so that errors would not be magnified in calculation.

To determine the contraction factor, the chemical equation at equilibrium must be derived. Take a mixture of 35 per cent. CO, 65 per cent. Air, and consider 100 vols of mixture before explosion :

$$35\,CO+13{\cdot}65\,O_2+51{\cdot}35\,N_2=A\,CO_2+B\,CO+D\,O_2+51{\cdot}3\,N_2.$$

We have immediately $A+B=35$ and $2A+B+2D=62{\cdot}3$.

The third equation is derived from the formula for K and the gas law :

$$K=\frac{B^2D\,P_0\,T_e}{A\,100\,T_0}\ (P_0 \text{ is initial press. in atmos. absolute}).$$

Choose a value for T_e the maximum temperature, and solve the equations by trial and error. The contraction factor is thus determined and the final temperature calculated, which must agree closely with the assumed temperature. It was found that, with mixtures of 45 per cent. gas and upwards, the dissociation was negligible and the contraction factor determined immediately.

TABLE II.

Initial Pressure, 2 atmospheres absolute.
Initial Temperature, 290° absolute.

Per cent. CO (pure).	Max. Temp.	Corrected Temp.	Per cent. Cooling loss.
20	1890 abs.	2305 abs.	25·9
25	2388	2544	10·95
30	2633	2692	5·35
35	2715	2757	4·20
40	2724	2772	3·29
45	2634	2695	2·71
49	2485	2543	3·03
53	2310	2395	4·71
58	1990	2150	9·89
62	1670	1976	20·55

In estimating the cooling correction it has been assumed that the heat lost by radiation up to the time of maximum pressure is small compared with the heat lost by conduction. According to David (Phil. Trans. 1912), this is justifiable in a silvered vessel. Then the actual heat lost to the walls should equal a constant times the product of temperature difference from flame to wall, and the time flame is in contact with the wall up to the maximum pressure. Considering any pressure curve, there is a bend over from the time the flame strikes the wall. If the walls were impervious to heat, the curve would have continued up. Similarly, the cooling curve may be produced back, and the intersection should give approximately the theoretical pressure. By this means the constant can be calculated for any particular mixture. It must be noted that this method is only applicable when dissociation is negligible, as in other cases the pressure curve does not show a true heat addition or cooling curve. Four such mixtures were available, 45 per cent., 50 per cent., 55 per cent., and 60 per cent. gas (97 per cent. purity). The actual and theoretical pressures and temperatures were obtained as already explained. Using Pier's values for the volumetric heats the heat evolved per grm. molecule is known, and the difference between the energies at these two temperatures is the heat loss to the wall. The time in seconds is known from the pressure curve and flame velocity, and the constant can be calculated. The maximum variation for these results was 10 per cent. about a mean value of 7·41. In view of the errors involved in producing the curves and the great differences in heat loss for the curves, this variation is quite good, and the mean constant was used for correcting all temperatures, the actual correction being the reverse process of the above. This reversal tends to eliminate any errors in Pier's results used.

The correction of mixtures which dissociate is rather complicated. The total heat evolved per gm. mol. is calculated as before, being the sum of the pressure energy and cooling loss. If there were no cooling this extra heat would not all appear as additional pressure energy, since more of the products would be dissociated at the higher temperature. The percentage of CO_2 formed at the lower temperature has already been calculated in determining this temperature. (Coefficient A in equilibrium equation.) By assuming the higher theoretical temperature, a new percentage of CO_2 is calculated, less than the previous one. The total heat evolved is then diminished in the ratio of these two percentages, and this heat used to calculate the theoretical temperature which must agree with that assumed. The extent of this correction can be seen in the case of the 30 per cent. mixture. The mean temperature calculated as above 2692° abs. If no allowance had been made for change of dissociation, the temperature would have been 2750° abs.

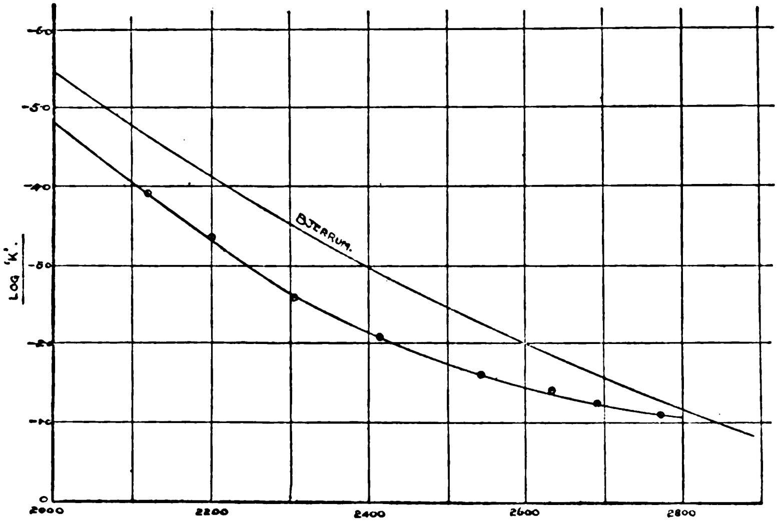
The cooling loss expressed as a percentage is the ratio of the heat loss to the wall to the total heat evolved by the gas up to the maximum pressure, after the temperature is lowered by cooling, and is given in Table II. It is remarkable that the percentage should vary so greatly for different mixtures of the same gases, being least for a rich mixture.

Sufficient information is now available for checking Pier's figures for volumetric heats, although the values for the different constituents cannot yet be separated. In order to eliminate any errors in dissociation, it is advisable to consider, as Pier did, only the maximum temperatures for rich mixtures, in which dissociation is negligible. In this case, it is found that the temperatures fall on a straight line, although no significance is attached to this at present. The calorific value for CO is taken at 68 kg.cals./gm. molecule, and from the proportion of CO_2 in the exhaust products the total heat of the exhaust is calculated, from which the mean volumetric heat is easily determined. At the higher temperatures, about 2700 abs., the agreement with Pier's values is very close, but for the lower temperatures the present results are higher than those of Pier. At 2066 abs. the values are 6·92 and 6·32 respectively for 60 per cent. CO mixture, while at 2713 the values are 7·32 and 7·21. This agreement of Pier's figures at very high temperatures was found by Bjerrum.

The amount of dissociation can also be calculated from the temperature curve, since two mixtures which give the same temperature must have the same percentage of carbon dioxide at equilibrium. On the rich side this composition is known, and hence for any dissociated mixture the amount of CO_2 formed can be calculated. The values of the equilibrium constants are then determined by the formula given. The values are shown plotted against those of Bjerrum in fig. 4. In correcting for cooling, Bjerrum makes no mention of the change in dissociation, so he presumably neglected this. If it is neglected in the present results, a curve is produced which agrees very closely with that of Bjerrum. The temperatures have all been worked out using Bjerrum's values, but, since the correction will only affect the contraction in volume, the temperatures will not be altered appreciably.

Fig. 4.

Variation of Equilibrium constants with Temperature.



Temperature—Absolute.

TABLE III.

Mixtures of Gas and Air at varying initial pressures.

CO per cent. (97·5 per cent. pure). Per cent.	Initial Press. lb./sq. in. abs.	Velocity. cm./sec.	Final Press. lb./sq. in. abs.	Press. Time. secs.	Press. Ratio.
25	14·7	97·7	94	·280	6·39
25	29·4	84·1	209·5	·385	7·12
25	44·1	69·7	313·5	·482	7·10
25	58·8	59·7	425	·550	7·22
25	73·5	49·0	543	·668	7·39
25	88·2	42·2	638	·990	7·24
25	102·9	37·2	768	1·01	7·47
30	29·4	107	231·5	·231	7·86
30	58·8	90·3	486	·335	8·25
30	88·2	76·4	780	·560	8·85

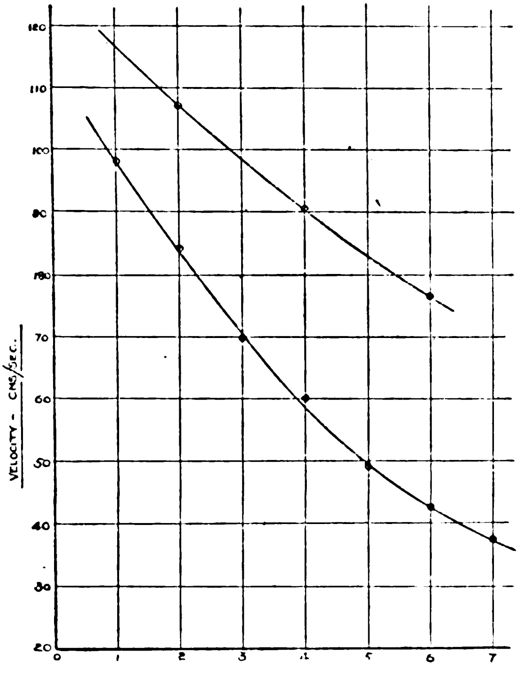
The effect of initial pressure on a mixture of CO and air is to greatly reduce the flame velocity and increase the time to reach maximum pressure. This is more pronounced in the case of the weaker mixtures. In addition at the higher pressures difficulties were experienced in exploding the mixtures, and in order to obtain records the gaps of the recording plugs in the sphere were decreased from 7 mm. at 1 atmosphere to 1½ mm. at 7 atmospheres. Bone (Proc. Roy. Soc. 1923–24) found a similar difficulty in exploding his mixtures at 50 atmospheres, and resorted to the fusing of a wire. Nagel carried out experiments with hydrogen and found a decrease in the time of combustion with increase in initial pressure, while some investigators using coal gas found an increase in combustion time, others found a decrease. The present results offer an explanation of the latter discrepancy, since the variation in flame velocity will doubtless depend upon the relative percentages of hydrogen and carbon monoxide in the coal gas. This emphasises the need for working with pure gases until these phenomena are understood.

This research confirms the work of others, that the lower limit of inflammability of CO and air is raised with increase of initial pressure. This does not explain why the velocity is lowered, but merely shifts the question. Bone attempts to explain his high-pressure work by an energy-absorbing property of nitrogen. In some later experiments he asserts that this is negligible below 10 atmospheres initial pressure, and so cannot account for the present reduction.

Since the velocity of hydrogen increases slightly, while that of CO decreases considerably, the explanation must be sought in the different chemical reaction. It is well known that for the combustion of CO the presence of water vapour is necessary, which is dissociated, the nascent oxygen oxidizing the CO. Thus the whole reaction may depend upon the rate of dissociation of water vapour. The law of mass action for a tri-molecular reaction shows that the percentage of oxygen dissociated will be roughly inversely proportional to the cube root of the absolute pressure. This rough agreement is found to exist between the pressure and flame velocity. This cannot be examined rigidly, as factors enter which cannot be definitely determined, but the explanation is put forward as a possible solution.

Fig. 5.

Variation of Velocity with Initial Pressure.



Initial Pressure—Atmos. Abs.

Experiments have been carried out with mixtures of CO_2, O_2, and N_2 at 2 atmospheres initial pressure, keeping the ratio of CO/O_2 constant at 1·97 to 1 and steadily decreasing the nitrogen content. At first the increase in velocity is proportional to the decrease in nitrogen, but afterwards the change in velocity becomes smaller and smaller. The results, on the whole, are very erratic. As the flame velocity increases, the oscillation of the flame front becomes very violent and of large amplitude. It is obvious for this particular size vessel that a point to point method is not suitable for velocity determinations above 200 cm./sec. Results, however, have been obtained by plotting from a large number of experiments and drawing a mean line. The following results serve to show the velocity increase :—

N_2 ...	56·5 per cent.	Velocity ...	107 cm./sec.
	42 „		199 „
	0 „	approx.	350 „

It is quite probable that when hydrogen is exploded in this vessel the same phenomenon will occur.

In addition, variations in maximum pressure and also time to reach maximum pressure occurred, both variations being in excess of likely errors in gas composition or water content.

As the nitrogen content is decreased, the time of combustion of an individual spherical shell also decreases, as determined by the two-point method previously explained. This became small enough to permit of two velocity determinations—that is, combustion had sufficiently decreased at the first gap before the flame struck the second. Ultimately, this could be obtained with two consecutive plugs whose radial distances differed by half an inch. In this case, with sufficient external gaps it would have been possible to have taken a complete velocity record at one explosion. Time, however, did not permit an attempt. As a confirmation of this, the point of inflexion disappeared from the pressure curve, which continued up to a sharp point when cooling set in. This sharp point also supports the assumption of an approach to chemical equilbrium as opposed to after-burning, apart from recombustion of dissociated products. This refers, of course, to a perfectly homogeneous mixture.

The following are the principal conclusions regarding the combustion of carbon monoxide at constant volume :—

(1) Flame velocity is at all times uniform, and in addition there is a regular vibratory motion at the flame front.

(2) Combustion is not complete when the flame strikes the wall of the explosion vessel. Instantaneous heat addition at any point can be approached under certain conditions, but probably never attained.

(3) Convection currents do not play a very important part, even in the weaker mixtures.

(4) The maximum velocity, pressure, and temperature occur with a rich mixture containing about 40 per cent. CO. The phenomena can be explained by dissociation.

(5) The percentage cooling loss is a minimum with a mixture of 45 per cent. CO and greatly increases as the upper and lower limits are approached.

(6) Pier's values for volumetric heats and Bjerrum's dissociation are slightly lower than values determined in this research.

(7) An increase of initial pressure greatly decreases the inflammability of CO and air.

(8) The effect of adding inert gas is to cause a slower flame velocity and a slower subsequent combustion.

For a fuller description of the foregoing research and details of calculations, etc., reference can be made to the original theses of the authors at the Birmingham University.

In conclusion, the two collaborators wish to express their thanks to Professor Burstall at the Mechanical Engineering Department of the University for his encouragement during the prosecution of this research.

CXIII. *The Whirling Speeds of Shafts carrying Concentrated Masses.* By R. C. J. Howland, *M.A.*, *M.Sc.*, *University College*, *London* *.

1. *Preliminary.*

THE whirling speeds of shafts carrying loads whose moments of inertia are negligible were considered by Dunkerley †, who gave a rule for computing the first whirling speed. His method consisted in finding the whirling speed for the case when all the loads but one were removed, and adding the squared reciprocals of the separate speeds found in this way. The sum was stated as the squared reciprocal of the whirling speed when all the loads were carried simultaneously. This rule, which was found to give approximately correct results in a number of cases, was without theoretical foundation, and its accuracy could be estimated only by experiment.

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* Communicated by Prof. L. N. G. Filon, M.A., D.Sc., F.R.S.

† Phil. Trans. A, clxxxv. (1894).

In a recent paper, Prof. H. H. Jeffcott* has given a theoretical derivation of Dunkerley's rule, by a method which enables all the whirling speeds of the loaded shaft to be computed to any desired degree of accuracy. The same method has been used by Hahn †.

The present paper attacks the problem from a different standpoint. Dunkerley's rule is arrived at by a theoretical method, which gives at the same time a correction term. A numerical estimate of the error involved in using the rule is made. The application of the method to non-uniform shafts is also considered.

2. *General Method of Computing Whirling Speeds.*

In the usual notation, the equation giving the deflexion of the shaft due to its rotation is

$$\frac{d^2}{dx^2}\left(\mathrm{EI}\frac{d^2y}{dx^2}\right) = m\omega^2 y, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where EI and m may both be functions of x. The discussion is a little simplified by writing the equation in its non-dimensional form. This is achieved by means of the substitutions,

$$\left.\begin{aligned} x &= lx', \\ y &= ly', \\ m &= \rho_0 \mathrm{A}_0 f(x'), \\ \mathrm{EI} &= \mathrm{E}_0 \mathrm{I}_0 \phi(x'), \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where l is the length of the shaft, and ρ_0, A_0, E_0, I_0 give the density, sectional area, elastic modulus, and second moment of section at some chosen point of the shaft. In what follows, they will be taken as referring to the end, $x=0$. If these substitutions are made, and the dashes then dropped, equation (1) is replaced by

$$\frac{d^2}{dx^2}\left(\phi(x)\frac{d^2y}{dx^2}\right) = \theta^4 f(x) y, \quad . \quad . \quad . \quad . \quad (3)$$

where

$$\theta^4 = \frac{\rho_0 \mathrm{A}_0 \omega^2 l^4}{\mathrm{E}_0 \mathrm{I}_0} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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* R. S. Proc. A, xcv. (1918).

† "Note sur la Vitesse Critique des Arbres et la Formule de Dunkerley," E. Hahn, *Schweizerische Bauzeitung*, Nov. 1918.

The whirling speeds are given by the critical values of θ^4 for which (3), together with the end conditions, give a value for y other than zero.

A method of solving equation (3) in powers of θ^4 was suggested by Messrs. Cowley and Levy *. It consists simply in assuming an expansion of this type and substituting in the equation. Equating powers of θ on the two sides results in a series of equations from which the coefficients may be found by integration.

Assume, then, that

$$y = y_0 + \theta^4 y_1 + \theta^8 y_2 + \ldots, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $y_0, y_1, y_2 \ldots$ are functions of x. Then we have at once from (3)

$$\left.\begin{aligned} \frac{d^2}{dx^2}\left(\phi(x)\frac{d^2y_0}{dx^2}\right) &= 0, \\ \frac{d^2}{dx^2}\left(\phi(x)\frac{d^2y_r}{dx^2}\right) &= f(x)y_{r-1}, \end{aligned}\right\} \quad . \quad . \quad . \quad (6)$$

from which $y_0, y_1 \ldots$ can be found successively by integration.

If the shaft is uniform, but carries masses which do not affect its elastic properties, $\phi(x)$ will be unity everywhere. The equations then reduce to

$$\left.\begin{aligned} \frac{d^4y_0}{dx^2} &= 0, \\ \frac{d^4y_r}{dx^2} &= f(x)y_{r-1}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and their solution is

$$\begin{aligned} y_0 = {} & \mathrm{A} + \mathrm{B}x + \mathrm{C}x^2 + \mathrm{D}x^3, \\ y_1 = {} & \mathrm{A}\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x)\,dx \\ & + \mathrm{B}\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x xf(x)\,dx \\ & + \mathrm{C}\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^2f(x)\,dx \\ & + \mathrm{D}\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^3f(x)\,dx, \end{aligned}$$

and so on;

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* "On a Method of Analysis suitable for the Differential Equations of Mathematical Physics," Phil. Mag. xli. April 1921.

or

$$y = \mathrm{A}f_1(x) + \mathrm{B}f_2(x) + \mathrm{C}f_3(x) + \mathrm{D}f_4(x), \quad . \quad . \quad (8)$$

where

$$\left.\begin{aligned}
f_1(x) = {} & \\
& 1 + \theta^4 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x)\, dx \\
& \quad + \theta^8 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x)\, dx \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x)\, dx \\
& \qquad + \text{etc.} \\
f_2(x) = {} & \\
& x + \theta^4 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x f(x)\, dx \\
& \quad + \theta^8 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x)\, dx \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x f(x)\, dx \\
& \qquad + \text{etc.} \\
f_3(x) = {} & \\
& x^2 + \theta^4 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^2 f(x)\, dx \\
& \quad + \theta^8 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x)\, dx \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^2 f(x)\, dx \\
& \qquad + \text{etc.} \\
f_4(x) = {} & \\
& x^3 + \theta^4 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^3 f(x)\, dx \\
& \quad + \theta^8 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x)\, dx \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^3 f(x)\, dx \\
& \qquad + \text{etc.}
\end{aligned}\right\} \quad . \quad . \quad . \quad (9)$$

Consider now a shaft with a short bearing at each end. Then

$$y = \frac{d^2y}{dx^2} = 0$$

when $x=0$ or 1. Substituting these values in (8) and using the obvious relations,

$$f_1(0) = 1, \qquad f_2(0) = f_3(0) = f_4(0) = 0,$$
$$f_1''(0) = f_2''(0) = f_4''(0) = 0, \qquad f_3''(0) = 2,$$

we have

$$\mathrm{A} = \mathrm{C} = 0$$

and

$$f_2(1)f_4''(1) = f_2''(1)f_4(1). \quad . \quad . \quad . \quad . \quad (10)$$

Similar equations may be found corresponding to other end conditions.

3. *Derivation of Dunkerley's Rule.*

When the shaft carries no additional masses, $f(x)$ reduces to unity at all points. The exact solution of (3) for this case is known, and the accuracy of the present method can be tested. In the series of equations (9) the coefficients are seen, in this case, to decrease with great rapidity, and this suggests that the lowest value of θ may be obtained approximately by neglecting all the powers of θ^4. The effect of including only the first two terms of the series in the case of a shaft carrying concentrated masses will now be examined.

Let the shaft have attached masses M_1, M_2, ... at distances a_1l, a_2l, ... from $x=0$; we then have $f(x)=1$ except for $x=a_1$, a_2, etc., while at these points

$$\lim_{\epsilon \to 0} \int_{a_r-\epsilon}^{a_r+\epsilon} f(x)\,dx = \frac{M_r}{\rho A l} = \mu_r. \quad . \quad . \quad . \quad (11)$$

Hence the required integrals are as follows:—

	$x > a_1$.	$x > a_2$.	
$\int_0^x xf(x)\,dx = \frac{1}{2}x^2$	$+\mu_1 a_1$	$+\mu_2 a_2$	+etc.
$\int_0^x dx \int_0^x xf(x)\,dx = \frac{1}{\underline{3}}x^3$	$+\mu_1 a_1(x-a_1)$	$+\mu_2 a_2(x-a_2)$	+etc.
$\int_0^x dx \int_0^x dx \int_0^x xf(x)\,dx = \frac{1}{\underline{4}}x^4$	$+\frac{1}{2}\mu_1 a_1(x-a_1)^2$	$+\frac{1}{2}\mu_2 a_2(x-a_2)^2$	+etc.
$\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x xf(x)\,dx = \frac{1}{\underline{5}}x^5$	$+\frac{1}{6}\mu_1 a_1(x-a_1)^3$	$+\frac{1}{6}\mu_2 a_2(x-a_2)^3$	+etc.
$\int_0^x x^3 f(x)\,dx = \frac{x^4}{4}$	$+\mu_1 a_1^3$	$+\mu_2 a_2^3$	+etc.
$\int_0^x dx \int_0^x f(x)x^3\,dx = \frac{x^5}{20}$	$+\mu_1 a_1^3(x-a_1)$	$+\mu_2 a_2^3(x-a_2)$	+etc.
$\int_0^x dx \int_0^x dx \int_0^x x^3 f(x)\,dx \quad \frac{x^6}{\underline{5}}$	$+\frac{1}{2}\mu_1 a_1^3(x-a_1)^2$	$+\frac{1}{2}\mu_2 a_2^3(x-a_2)^2$	+etc.
$\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^3 f(x)\,dx = \frac{6x^7}{\underline{\vert 7}}$	$+\frac{1}{6}\mu_1 a_1^3(x-a_1)^3$	$+\frac{1}{6}\mu_2 a_2^3(x-a_2)^3$	+etc.

Hence

$$\left.\begin{aligned}
\int_0^1 dx \int_0^x xf(x)\,dx &= \frac{1}{6} + \sum_{r=1}^{n} \mu_r a_r b_r, \\
\int_0^1 dx \int_0^x dx \int_0^x dx \int_0^x xf(x)\,dx &= \frac{1}{\underline{|5}} + \frac{1}{6}\sum_{r=1}^{n} \mu_r a_r b_r^3, \\
\int_0^1 dx \int_0^x x^3 f(x)\,dx &= \frac{1}{20} + \sum_{r=1}^{n} \mu_r a_r^3 b_r, \\
\int_0^1 dx \int_0^x dx \int_0^x dx \int_0^x x^3 f(x)\,dx &= \frac{6}{\underline{|7}} + \frac{1}{6}\sum_{r=1}^{n} \mu_r a_r^3 b_r^3,
\end{aligned}\right\} \quad (12)$$

$$\text{where} \qquad b_r = 1 - a_r.$$

If terms in θ^8 are neglected, we therefore have

$$\left.\begin{aligned}
f_2\,(1) &= 1 + \theta^4\left[\frac{1}{\underline{|5}} + \frac{1}{6}\sum_{r=1}^{n} \mu_r a_r b_r^3\right], \\
f_2''(1) &= \theta^4\left[\frac{1}{6} + \sum_{r=1}^{n} \mu_r a_r b_r\right], \\
f_4\,(1) &= 1 + \theta^4\left[\frac{6}{\underline{|7}} + \frac{1}{6}\sum_{r=1}^{n} \mu_r a_r^3 b_r^3\right], \\
f_4''(1) &= 6 + \theta^4\left[\frac{1}{20} + \sum_{r=1}^{n} \mu_r a_r^3 b_r\right].
\end{aligned}\right\} \quad . \quad . \quad (13)$$

Substituting these values in (10) and again neglecting a term in θ^8,

$$6 + \theta^4\left[\frac{1}{10} + \sum_{r=1}^{n} \mu_r (a_r^3 b_r + a_r b_r^3)\right]$$

$$= \theta^4\left[\frac{1}{6} + \sum_{r=1}^{n} \mu_r a_r b_r\right],$$

$$\text{or} \qquad 6 = \theta^4\left[\frac{1}{15} + \sum_{r=1}^{n} \mu_r a_r b_r (1 - a_r^2 - b_r^2)\right]$$

$$= \theta^4\left[\frac{1}{15} + 2\sum_{r=1}^{n} \mu_r a_r^2 b_r^2\right],$$

$$\text{since} \qquad a_r^2 + b_r^2 + 2a_r b_r = 1.$$

Hence
$$\theta^4 = \frac{6}{\frac{1}{15} + 2\sum_{r=1}^{n} \mu_r a_r^2 b_r^2}$$

and
$$\left.\begin{aligned} \omega^2 &= \frac{3\mathrm{EI}}{\rho \mathrm{A} l^4 \sum_{r=0}^{n} \mu_r a_r^2 b_r^2}, \\ \text{where} \quad \mu_0 a_0^2 b_0^2 &= \frac{1}{30}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (14)$$

The mass of the shaft is taken as equivalent to a concentrated mass $\frac{8}{15}\rho \mathrm{A} l$ placed at the mid-point.

If ω_0 be the lowest whirling speed for such a mass when the other loads are removed, and if $\omega_1, \omega_2, \ldots \omega_n$ be the whirling speeds due to each of the separate masses acting alone on a mass-less shaft, (14) is equivalent to

$$\frac{1}{\omega^2} = \frac{1}{\omega_0^2} + \frac{1}{\omega_1^2} + \ldots + \frac{1}{\omega_n^2}, \quad . \quad . \quad . \quad (15)$$

which is Dunkerley's rule.

The occurrence of (15) depends only on the neglect of powers of θ^4, and Dunkerley's rule would result whatever the end conditions and whether the shaft is uniform or of varying section.

It is, however, by no means obvious that the neglect of the higher terms is justified, for θ is, in most cases, not a small quantity. Thus, for a uniform shaft, $\theta = \pi$. The assumption made is, therefore, that the coefficients of higher powers of θ are extremely small, and this will only be the case if the whirling speeds form a sequence in which the terms increase rapidly. It is thus evident that Dunkerley's rule is quite without justification until the magnitude of the other coefficients in the series has been examined.

4. *The Error in Dunkerley's Rule* *.

For a uniform unloaded shaft the above method gives

$$\omega^2 = \frac{90\,\mathrm{EI}}{\rho \mathrm{A} l^4},$$

as compared with the value

$$\omega^2 = \frac{\pi^4\,\mathrm{EI}}{\rho \mathrm{A} l^4}$$

given by the ordinary method of analysis.

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* *Cf.* Hahn, *loc. cit.*

The value of ω is therefore too low in the ratio

$$\sqrt{90} : \pi^2 = 0{\cdot}96 : 1,$$

an error of 4 per cent.

In this simple case it is easy to extend the series to the θ^8 term. The equation then becomes

$$6 - \tfrac{1}{15}\theta^4 + {\cdot}0000526\,\theta^8 = 0.$$

This gives as a second approximation

$$\begin{aligned} \theta^4 &= 90 + {\cdot}000789\,\theta^8 \\ &= 90 + {\cdot}000789 \times 90^2 \\ &= 96{\cdot}39. \quad \dots\dots\dots \quad (16) \end{aligned}$$

Using this figure to obtain a closer approximation, we have

$$\begin{aligned} \theta^4 &= 90 + {\cdot}000789 \times (96{\cdot}4)^2 \\ &= 97{\cdot}3 \quad \text{approx.} \quad \dots\dots \quad (17) \end{aligned}$$

This gives $\theta^4 = \pi^4$ exactly, to the number of figures taken.

Thus the inclusion of the third term is sufficient for accuracy, but if it is used only to give a second approximation, such as (16), the value of θ^4 is too low by about 1 per cent.

The magnitude of the third term in the series will now be investigated for the case when the shaft carries concentrated loads. To simplify the analysis, the mass of the shaft itself will be neglected.

If $\psi(x)$, $\chi(x)$ denote the integrals

$$\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x f(x)\, dx$$

and

$$\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^3 f(x)\, dx,$$

the values of these functions, when only concentrated loads are taken into account, are

$$\begin{array}{r|c|c|c|l} & \underline{x < a_1.} & \underline{x > a_1.} & \underline{x > a_2.} & \\ \psi(x) = & 0 & +\frac{1}{6}\mu_1 a_1 (x - a_1)^3 & +\frac{1}{6}\mu_2 a_2 (x - a_2)^3 & + \text{etc.} \\ \chi(x) = & 0 & +\frac{1}{6}\mu_1 a_1^3 (x - a_1)^3 & +\frac{1}{6}\mu_2 a_2^3 (x - a_2)^3 & + \text{etc.} \end{array}$$

Also $f(x)=0$, except at $x=a_r$, $r=1, 2, \dots n$, and

$$\underset{\epsilon\to 0}{\mathrm{Lim}} \int_{a_r-\epsilon}^{a_r+\epsilon} f(x)\,dx = \mu_r.$$

The following integrals are now required:—

		$x<a_2$.	$x>a_2$.	$x>a_3$.	
$\int_0^x \psi(x)f(x)\,dx$	=	0	$+\frac{1}{6}\mu_1\mu_2a_1(a_2-a_1)^3$	$+\frac{1}{6}\mu_1\mu_3a_1(a_3-a_1)^3$	+etc.
				$+\frac{1}{6}\mu_2\mu_3a_2(a_3-a_2)^3$	+etc.
					+etc.
$\int_0^x dx\int_0^x \psi(x)f(x)\,dx$	=	0	$+\frac{1}{6}\mu_1\mu_2a_1(a_2-a_1)^3$ $(x-a_2)$	$+\frac{1}{6}\mu_1\mu_3a_1(a_3-a_1)^3$ $(x-a_3)$	+etc.
				$+\frac{1}{6}\mu_2\mu_3a_2(a_3-a_2)^3$ $(x-a_3)$	+etc.
					+etc.
$\int_0^x dx\int_0^x dx\int_0^x dx\int_0^x \psi(x)f(x)\,dx$	=	0	$+\frac{1}{36}\mu_1\mu_2a_1(a_2-a_1)^3$ $(x-a_2)^3$	$+\frac{1}{36}\mu_1\mu_3a_1(a_3-a_1)^3$ $(x-a_3)^3$	+etc.
				$+\frac{1}{36}\mu_2\mu_3a_2(a_3-a_2)^3$ $(x-a_3)^3$	+etc.
					+etc.

Hence

$$\int_0^1 dx\int_0^x \psi(x)f(x)\,dx$$
$$= \frac{1}{6}\sum_{r=1}^{n-1}\sum_{s=r+1}^{n} \mu_r\mu_s a_r(a_s-a_r)^3(1-a_s),$$

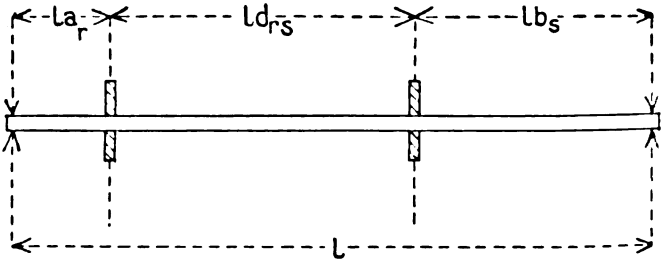
$$\int_0^1 dx\int_0^x dx\int_0^x dx\int_0^x \psi(x)f(x)\,dx$$
$$= \frac{1}{36}\sum_{r=1}^{n-1}\sum_{s=r+1}^{n} \mu_r\mu_s a_r(a_s-a_r)^3(1-a_s)^3.$$

These may conveniently be written as follows:—

$$\left.\begin{aligned}\int_0^1 dx\int_0^x \psi(x)f(x)\,dx &= \frac{1}{6}\sum_{r,s=1}^{n} \mu_r\mu_s a_r b_s d_{rs}^3,\\ \int_0^1 dx\int_0^x dx\int_0^x dx\int_0^x \psi(x)f(x)\,dx &= \frac{1}{36}\sum_{r,s=1}^{n} \mu_r\mu_s a_r b_s^3 d_{rs}^3,\end{aligned}\right\} \quad (18)$$

where ld_{rs} is the distance between the two loads, and the summation is for all pairs of loads in the relative positions shown in fig. 1.

Fig. 1.



In a similar way,

$$\left.\begin{aligned}\int_0^1 dx\int_0^x \chi(x)f(x)\,dx &= \tfrac{1}{6}\sum_{r,s=1}^{n}\mu_r\mu_s a_r^3 b_s d_{rs}^3,\\ \int_0^1 dx\int_0^x dx\int_0^x dx\int_0^x \chi(x)f(x)\,dx &= \tfrac{1}{36}\sum_{r,s=1}^{n}\mu_r\mu_s a_r^3 b_s^3 d_{rs}^3.\end{aligned}\right\}\quad(19)$$

Hence, including the θ^8 terms,

$$\left.\begin{aligned}f_2\,(1) &= 1+\tfrac{1}{6}\theta^4\sum_{r=1}^{n}\mu_r a_r b_r^3+\tfrac{1}{36}\theta^8\sum_{r,s=1}^{n}\mu_r\mu_s a_r b_s^3 d_{rs}^3,\\ f_2''(1) &= \theta^4\sum_{r=1}^{n}\mu_r a_r b_r+\tfrac{1}{6}\theta^8\sum_{r,s=1}^{n}\mu_r\mu_s a_r b_s d_{rs}^3,\\ f_4\,(1) &= 1+\tfrac{1}{6}\theta^4\sum_{r=1}^{n}\mu_r a_r^3 b_r^3+\tfrac{1}{36}\theta^8\sum_{r,s=1}^{n}\mu_r\mu_s a_r^3 b_s^3 d_{rs}^3,\\ f_4''(1) &= 6+\theta^4\sum_{r=1}^{n}\mu_r a_r^3 b_r+\tfrac{1}{6}\theta^8\sum_{r,s=1}^{n}\mu_r\mu_s a_r^3 b_s d_{rs}^3,\end{aligned}\right\}\quad(20)$$

and the equation for the whirling speed is

$$\begin{aligned}6-\theta^4\sum_{r=1}^{n}\mu_r(a_r b_r-a_r^3 b_r-a_r b_r^3)\\ +\theta^8\Big[\tfrac{1}{6}\sum_{r=1}^{n}\mu_r a_r b_r^3\sum_{r=1}^{n}\mu_r a_r^3 b_r-\tfrac{1}{6}\sum_{r=1}^{n}\mu_r a_r b_r\sum_{r=1}^{n}\mu_r a_r^3 b_r^3\\ -\tfrac{1}{6}\sum_{r,s=1}^{n}\mu_r\mu_s(a_r b_s-a_r b_s^3-a_r^3 b_s)\,d_{rs}^3\Big]=0,\quad .\quad(21)\end{aligned}$$

or

$$1-\tfrac{1}{6}\theta^4\sum_{r=1}^{n}2\mu_r a_r^2 b_r^2$$

$$+\tfrac{1}{36}\theta^8\sum_{r,s=1}^{n}\mu_r\mu_s a_r b_s\{a_s b_r(a_s^2-a_r^2)(b_r^2-b_s^2)$$

$$-(1-a_r^2-b_s^2)d_{rs}^3\}=0, \quad (22)$$

where, in the last term, the summation includes each pair of masses once only.

If (22) is written

$$1-\tfrac{1}{6}p\theta^4+\tfrac{1}{36}q\theta^8=0, \quad . \quad . \quad . \quad . \quad (23)$$

the second approximation to the least value of θ is given by

$$\theta^4=\frac{6}{p}+\frac{q}{6p}\theta^8$$

$$=\frac{6}{p}\left(1+\frac{q}{p^2}\right). \quad . \quad . \quad . \quad . \quad . \quad (24)$$

The magnitude of the correction given by the term $\frac{q}{p^2}$ is shown in the following table for the case when the masses are equal and equally spaced :—

No. of Masses.	Value of $\frac{q}{p^2}$.	Percentage change in value of ω made by including this term.
2	·0586	nearly 3 per cent.
3	·0675	„ 3·5 „ „
4	·0698	„ 3·5 „ „
5	·0707	about 3·5 „ „
6	·0709	„ 3·5 „ „
7	·071	„ 3·5 „ „
9	·071	„ 3·5 „ „
∞	·071	„ 3·5 „ „

The last value has been obtained by expressing the limiting value of $\frac{q}{p^2}$, as given by (22), in the form of a double integral. The result, as might be expected, is identical with that given by the analysis leading to equation (16).

The remarkable thing about these figures is the rapidity with which the limiting value is approached as n increases, so that the correction is systematically in the neighbourhood of 3·5 per cent.

As in the case of the uniform shaft, this correction is raised to 4 per cent. by carrying the approximation a stage further. We have, in fact, from the equation

$$\theta^4 = \frac{6}{p} + \frac{q}{6p}\theta^8$$

the approximate value

$$\theta^4 = \frac{6}{p}\left(1 + \frac{q}{p^2} + \frac{2q^2}{p^4} + \frac{q^3}{p^6}\right)$$

$$= \frac{6}{p}(1{\cdot}0814),$$

when q/p^2 has the value ·071. This gives the correction of 4 per cent. which, accurate in the case of a uniform mass, will be very nearly so for concentrated masses *.

A revised form of the rule can now be given from the consideration that, if a multiplier is introduced which corrects the term due to the mass of the shaft itself, the whole expression will be simultaneously corrected, to a fair degree of approximation. Thus for a shaft carrying concentrated masses, the mass of the shaft itself not being negligible, the first whirling speed is given by

$$\frac{a}{\omega^2} = \frac{1}{\omega_0^{\,2}} + \sum_{r=1}^{r=n} \frac{1}{\omega_r^{\,2}}, \quad . \quad . \quad . \quad . \quad . \qquad (25)$$

where a, $\omega_0^{\,2}$, $\omega_r^{\,2}$ are given for various types of support in the table below. All the values are obtainable by analysis similar to the above.

Type of Bearings.	a^2.	$\omega_0^{\,2}$.	$\omega_r^{\,2}$.
Both short	1·08	$90EI/\rho A l^4$	$3EIl/m_r a_r^2 b_r^2$
Both long	1·168	$420EI/\rho A l^4$	$3EIl^3/m_r a_r^3 b_r^3$
One short, one long †	1·12	$210EI/\rho A l^4$	$12EIl^3/m_r a_r^3 b_r^2(3a_r + 4b_r)$
One long, shaft overhangs ...	1·017	$12EI/\rho A l^4$	$3EI/m_r a_r^3$

† $a_r l$ is here the distance from the long bearing.

When the attached masses divide the shaft into unequal segments, the error in Dunkerley's rule will be found in

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* This limiting value of the correction is given by Hahn in the paper cited above. He does not, however, examine the convergence towards the limit.

general to be rather less than for the same number of equally placed masses. The variation in the error when only two masses are carried and one is moved along the shaft, the other remaining fixed, has been studied by Hahn *, who has also considered the effect of the finite size of the masses.

5. *Non-Uniform Shaft.*

If I_0 be the moment of inertia of the section at $x=0$, and if $\frac{I}{I_0}=\phi(x)$, the equation for y becomes

$$\frac{d^2}{dx^2}\left(\phi(x)\frac{d^2y}{dx^2}\right)-\theta^4 f(x)y=0, \quad . \quad . \quad . \quad (26)$$

where

$$\theta^4=\frac{\rho A\omega^2 l^4}{EI_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

The solution of equation (26) is easily seen to be

$$\left.\begin{aligned}
&y = Af_1(x)+Bf_2(x)+Cf_3(x)+Df_4(x),\\
&\text{where}\\
&f_1(x) = 1+\theta^4\int_0^x dx\int_0^x\frac{dx}{\phi(x)}\int_0^x dx\int_0^x f(x)\,dx+\dots,\\
&f_2(x) = x+\theta^4\int_0^x dx\int_0^x\frac{dx}{\phi(x)}\int_0^x dx\int_0^x xf(x)\,dx+\dots,\\
&f_3(x) = \int_0^x dx\int_0^x\frac{dx}{\phi(x)}\\
&\qquad +\theta^4\int_0^x dx\int_0^x\frac{dx}{\phi(x)}\int_0^x dx\int_0^x f(x)\,dx\int_0^x dx\int_0^x\frac{dx}{\phi(x)}+\text{etc.}\\
&f_4(x) = \int_0^x dx\int_0^x\frac{x\,dx}{\phi(x)}\\
&\qquad +\theta^4\int_0^x dx\int_0^x\frac{dx}{\phi(x)}\int_0^x dx\int_0^x f(x)\,dx\int_0^x dx\int_0^x\frac{x\,dx}{\phi(x)}.
\end{aligned}\right\} \quad . \quad . \quad . \quad (28)$$

In these, let $\phi(x)$ be any function, while $f(x)$ is zero except at special points.

To obtain the first approximation it is sufficient to consider a shaft carrying only one load. If the ends are in short bearings, the end conditions will lead to equation (10), as before. The values of the functions involved are, neglecting θ^8,

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* *Loc. cit.*

$$\left.\begin{aligned}
f_2\ (1) &= 1+\mu a\theta^4\int_a^1 dx\int_a^x \frac{(x-a)}{\phi(x)}\,dx,\\
f_2''(1) &= \frac{\mu a\theta^4(1-a)}{\phi(1)},\\
f_4\ (1) &= \int_0^1 dx\int_0^x \frac{dx}{\phi(x)}+\mu\theta^4\int_a^1 dx\int_a^x \frac{x-a}{\phi(x)}\,dx\times\int_0^a dx\int_0^x \frac{x\,dx}{\phi(x)},\\
f_4''(1) &= \frac{1}{\phi(1)}\left[1+\mu(1-a)\int_0^a dx\int_0^x \frac{x\,dx}{\phi(x)}\right].
\end{aligned}\right\} \quad . \quad . \quad . \quad (29)$$

When these are substituted in (10), the equation for θ^4 is

$$\mu\theta^4\left[ab\int_0^1 dx\int_0^x \frac{dx}{\phi(x)}-a\int_a^1 dx\int_a^x \frac{x-a}{\phi(x)}\,dx-b\int_0^a dx\int_0^x \frac{x\,dx}{\phi(x)}\right]=1. \quad . \quad . \quad . \quad (30)$$

It is not difficult to verify that the quantity in the bracket is equal to

$$\frac{\mathrm{EI}_0}{l^4}\delta,$$

where δ is the deflexion that would be caused at the position of the load by a transverse unit force acting there on the shaft. Hence

$$\omega^2 = \frac{1}{\mathrm{M}\delta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

as is otherwise evident.

If the series is carried to the term in θ^8, a correction term is obtained equivalent to that given by Prof. Jeffcott's analysis. The advantage of the present method is that it enables concentrated loads and distributed loads to be treated together.

From the analogy of the uniform shaft, it is likely that the θ^8 term will give almost the whole of the correction needed for the first whirling speed, and that the corrections needed when the shaft carries concentrated loads will not be very different from those required for distributed loads.

The following method is therefore suited to give the first whirling speed of a non-uniform shaft carrying concentrated masses in addition to a distributed load :—

(1) By means of equations (28), let first and second approximations to the whirling speeds be found when the concentrated masses are removed. Let the first approximation be ω_0, and the second, which will be nearly exact, $a\omega_0$.

(2) From (30) find ω_r^2 for each concentrated load.

(3) The whirling speed is then given by

$$\frac{a^2}{\omega^2}=\frac{1}{\omega_0^2}+\sum_{r=1}^{n}\frac{1}{\omega_r^2}. \quad . \quad . \quad . \quad . \qquad (25\text{ bis})$$

CXIV. *The Magnetic Properties of Atoms and Molecules.*

By Bernard Howell Wilsdon *.

In two previous papers (*suprà*, pp. 354, 900) a theory of the polar and non-polar chemical link has been developed on the basis of quantum exchanges between valency orbits involving half numbers. The non-polar link was treated in a manner similar to that which was successfully employed by Sommerfeld in explaining the anomalous Zeeman effect. The polar link was attacked from the standpoint of the Stark effect. In both treatments the fundamental postulate was adopted that precessional or nutational movements of the orbits which form the chemical bond synchronize the frequencies of the naturally untuned orbits, in a manner whereby the total moment of momentum in opposite directions of the bond is equalized. By this means, with simple and consistent assumption as to quantum changes, the heats of formation of various simple bodies were calculated and reasonably good agreement with experimental values was obtained. The application of the fundamental postulate of the synchronization of frequencies, together with the principle of spatial quantizing, should enable us to draw definite and quantitative conclusions as to the magnetic and stereometric properties of the molecule. In calculating the energy changes consequent on combinations of atoms, we assumed that the component of the moment of momentum in a direction at right angles to "the equatorial plane" of the molecule must be equal and opposite for each atom. The residual moments of the valency electron or electrons must then all lie along axes which lie in the equatorial plane. The two halves of the molecule must behave as rigid systems, since by spatial quantizing the inclination as well as the size of the orbits is fixed. The orientation of the axes which lie in the equatorial plane is, of course, not subject to spatial quantizing; they are free to rotate about the molecular axis, so long as their inclination thereto does not change. Since no energy change is involved in such displacements, the orientation of such axes will be determined by probability considerations.

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* Communicated by the Author.

Synchronization of the orbital movements of the electrons belonging to different parts of the molecule will be brought about by precessional rotations in opposite senses of the systems. It is these rotations which bring the moments of the two systems into equilibrium. No assumption need be made as to a necessary equality in the number of valency orbits associated with each atom in combination, nor is it necessary to suppose that the electrons of the different atoms move in joint orbits. So long as the axial components of the moments are equal and opposite on both sides of the equatorial plane, and the rotations of the electrons in their orbits synchronize, the conditions for chemical combination are fulfilled. As an example of the arrangement of orbits postulated, we may take the case of nitric oxide. Four electrons of each atom belonging to the k_1 group may lock up together into a configuration of zero moment similar to the valency shell surrounding a rare gas. This leaves two k_2 orbits belonging to the oxygen, and one for the nitrogen. Alternatively we may suppose that five electrons from the oxygen and one from the nitrogen lock up, leaving one free oxygen valency and three free nitrogens. The underlying group of six electrons in this case corresponds to one of the stable sub-groups shown by Bohr's well-known arrangement. Equilibrium across the equatorial plane would then be obtained by orientating $3(k=3/2)$ nitrogen electrons at $\cos\theta=1/3$ and $1(k=3/2)$ oxygen electron at $\cos\theta=1$. It may be expected that such an arrangement will give rise to a free moment, as is found to be the case. It will be shown that models of this character will give quantitative explanations of the magnetic properties of atoms and molecules on the basis of the simple assumptions outlined above.

For simplicity we regard the electrons as occupying their time mean positions in their Kepler orbits. These orbits will precess in the molecular magnetic field, so the problem will reduce itself to calculating the moment of the system in its rotations about the precessional axis. Since the system is rigid, if we take a point of reference which is fixed in space and which we may regard as situated in one or other of the atomic nuclei, it is easy to deduce from d'Alembert's principle that

$$\frac{d\mathbf{q}'}{dt}=\mathrm{V}\mathbf{pq}-\mathbf{L}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here the **p**'s are the moments of momenta and the **q**'s are angular velocities; **L** is the mechanical moment. **q**$'$ is a velocity referred to an origin which rotates with the rigid system. $d\mathbf{q}'/dt$ must be equal to zero; so we may write

$$\mathrm{V}\mathbf{pq}=\mathbf{L}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since the **p**'s and **q**'s must necessarily be related, we may introduce an operator which transforms the vector **q** into **p**. This operator may be written as the sum of a symmetrical linear operator and the vector product of another vector **f**, so that

$$\mathbf{p}=\Omega\mathbf{q}+\mathrm{V}\mathbf{fq}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Equation (2) may thus be written:

$$\mathbf{L}=\mathbf{q}\Omega\mathbf{q}+\mathrm{V}\mathbf{q}\mathrm{V}\mathbf{fq}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Since **L** is a vector magnitude, it must be related to the resultant magnetic moment of the molecule and the field as follows:

$$\mathbf{L}=\mathrm{V}\mu\mathbf{H}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If we consider an isolated molecule for which we have fixed in space a point of reference in one of its nuclei, its paramagnetism must be a vector quantity determined by the intrinsic properties of the molecular structure. A diamagnetic molecule, on the other hand, only develops a magnetic moment when we also determine the direction and magnitude of an external field. This is seen at once from equation (4), for since Ω is symmetrical, the first term is zero, so that the free moment is zero in the absence of an external field. The "susceptibility" of a molecule measures the rate of change of the magnetic moment with the strength of an imposed magnetic field. For a fixed paramagnetic molecule the susceptibility should therefore be zero, since its free moment is not dependent on the strength of the field (this assumes, of course, that we are dealing with a simple molecule composed of only two atoms). The susceptibility, so called, of a paramagnetic substance as measured in the gaseous or liquid state will thus be a probability function of the temperature which may be written $\frac{\mu}{\mathrm{H}}\frac{\partial\mathbf{x}}{\partial\mathbf{y}}$ where **x** and **y** are unit vectors determining the directions of the magnetic moment and field respectively. For a diamagnetic molecule, on the other hand, we measure the quantity $\frac{\mathbf{x}}{\mathbf{y}}\frac{\partial\mu}{\partial \mathrm{H}}$, where $\frac{\partial\mu}{\partial \mathrm{H}}$ will be an intrinsic property of the molecule and $\frac{\mathbf{x}}{\mathbf{y}}$ fixed by probability considerations. Since no particular direction in a simple diamagnetic molecule will be favoured in a random assemblage, this function will be a constant independent of the temperature, so long as the electronic structure does not undergo a change, as is well known to be the case in most simple substances.

In order to obtain an expression for the diamagnetism of the molecule, we may proceed as follows:—

Multiplying (4) by the Hamiltonian operator, we have

$$\nabla \mathrm{V}\mu\mathbf{H} = \nabla \mathrm{V}\mathbf{q}\mathrm{V}\mathbf{f}\mathbf{q} + \nabla \mathrm{V}\mathbf{q}\Omega\mathbf{q},$$

so that

$$\mathbf{H}\ \mathrm{curl}\ \mu = \mathrm{V}\mathbf{f}\mathbf{q}\ \mathrm{curl}\ \mathbf{q} + \Omega\mathbf{q}\ \mathrm{curl}\ \mathbf{q} - \mathbf{q}\ \mathrm{curl}\ \Omega\mathbf{q}.$$

$\Omega\mathbf{q}\ \mathrm{curl}\ \mathbf{q}$ is equal to zero; if we limit consideration first to a symmetrical molecule, we may ignore $\mathrm{V}\mathbf{f}\mathbf{q}$ and write

$$\mathbf{H}\ \mathrm{curl}\ \mu = -\mathbf{q}\ \mathrm{curl}\ \Omega\mathbf{q}. \quad . \quad . \quad . \quad . \quad (6)$$

Now a precessional rotation $\mathbf{O}$ is related to a vector magnetic field by the well-known Lorentz expression

$$\mathbf{O} = \frac{e\mathbf{H}}{2mc}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The angular velocity of our rotating rigid system $\mathbf{q}$ may thus be equated to $\mathbf{O}$.

Substituting (7) in (6), we then have

$$\mathbf{H}\ \mathrm{curl}\ \mu = -\frac{e\mathbf{H}}{2mc}\ \mathrm{curl}\ \Omega\mathbf{q}$$

or

$$\mu = -\frac{e}{2mc}\Omega\mathbf{q}.$$

Writing $\mathbf{q}$ as the product of a scalar q into the unit vector $\mathbf{x}$ and again substituting (7), we have

$$\mu = -\frac{e^2}{4m^2c^2}\mathbf{H}\Omega\mathbf{x} = -\frac{e^2}{4m^2c^2}\mathrm{H}\mathbf{y}\Omega\mathbf{x},$$

where $\mathbf{y}$ is a unit vector defining $\mathbf{H}$, so that

$$\frac{\partial\mu}{\partial \mathrm{H}} = -\frac{e^2}{4m^2c^2}\mathbf{y}\Omega\mathbf{x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In order to calculate the paramagnetism, (4) may be written, since $V\mathbf{q}\Omega\mathbf{q}$ is zero,

$$\mu H V\mathbf{xy} = (q^2)\mathbf{f} - (\mathbf{qf})\mathbf{q}.$$

The direction of the atomic or molecular field **H** must be the same as that of the resultant angular velocity **q**, so that

$$\mu H = q^2\mathbf{f}V\mathbf{xy} - (\mathbf{qf})\mathbf{q}V\mathbf{xy}. \quad . \quad . \quad . \quad . \quad (9)$$

The last term of this equation is zero, since the vector product $V\mathbf{xy}$ is at right angles to the direction of **q**. This follows from the consideration that the internal field of the paramagnetic molecule must be in the same direction as the vector which determines the axis of the angular velocity **q**. Dividing by H^2 from (7), we then have

$$\frac{\mu}{H} = \frac{e^2}{4m^2c^2}\,\mathbf{f}V\mathbf{xy} = \frac{e^2}{4m^2c^2}\,\mathbf{y}V\mathbf{fx}. \quad . \quad . \quad . \quad (10)$$

Multiplying by **y**, we see at once that the free moment μ is at right angles to the direction of **x**.

We have now to develop the operators Ω and $V\mathbf{f}$. Their form may be seen from the following simple considerations. The moment of momentum p is equal to $\Sigma \frac{dE_{\text{kin}}}{dq}$. Considering for simplicity that the electrons of the precessing orbits are fixed in their time mean positions, we may write for the kinetic energy due to their precessional movements

$$E_{\text{kin}} = \Sigma \frac{m}{2}(\dot{r}^2 + r^2q^2).$$

The time mean value of $\dot{r}$ is zero, so

$$p = \Sigma \frac{m}{2} r^2 \frac{dq^2}{dq} = \Sigma mr^2q.$$

The operators are thus of the form Σmr^2. This means that we have to deal with an "inertial" operator as in the ordinary case of Poinsot motion. The time mean displacements can now be calculated in terms of the azimuthal and principal quantum numbers of the orbits. It has been shown (*cf.* Sommerfeld, 'Atomic Structure,' Eng. trans. p. 313) that $r = 3/2a\epsilon$, where a is the major axis of the Kepler ellipse and ϵ is the eccentricity. The eccentricity is given by the factor

$$\epsilon = \sqrt{1 - \frac{k^2}{n^2}},$$

where n and k represent the principal and azimuthal quantum numbers respectively. r thus becomes equal to

$$r=\frac{3}{2}\frac{h^2}{4\pi^2 me^2 Z}.n\sqrt{n^2-k^2}, \quad . \quad . \quad . \quad . \quad (11)$$

where Z is the effective atomic number.

In what follows we consider only the inertia components of the valency electrons. By neglecting the inertias of the nucleus and inner electrons we shall not make a great error. The energy of the nucleus can only represent a small heat term; a quantum group in the shell next below the valency rings, when complete, must be symmetrical, and thus will not contribute to the inertia terms. This is not the case when the shell next below the valency shell is incomplete, as it is in the transition elements; it will be shown later that the strong paramagnetism of these elements is to be attributed to this fact. Since then the mass term of our inertial operator is constant and equal to that of the electron, we need consider only the squares of the time mean displacements r^2. Call these R_i; for each orbit there will then correspond an axis which we assume is uniquely occupied for the reason that two orbits, orientated in the same direction and belonging to the same atom but having different parameters, would inevitably entail a collision when subjected to an external field. Moreover, we have no reasons for assuming that the same orbit can be occupied by two electrons. We may then choose for convenience as many axes, $\mathbf{x}_1$, $\mathbf{x}_2$, $\mathbf{x}_3$ . . . $\mathbf{x}_i$, as there are active valency electrons in the atom. If we distinguish one of them, $\mathbf{x}_1$, as that normal to the equatorial plane of the molecule, it will be convenient to place the remainder on the equatorial plane. We may now write the two operators Ω and $V\mathbf{f}$ in terms of conjugate components R and R′, where Ω is the arithmetical mean of R and R′. R and R′ must be identified in our present case with the inertial components on either side of the same axis; but since we assume constantly that the sense of the rotation reverses on either side of the axis, we shall write

$$\Omega=\tfrac{1}{2}(R-R').$$

$\Omega\mathbf{x}$ then becomes simply

$$\tfrac{1}{2}\{\mathbf{x}_1(R_1-R_1')+\mathbf{x}_2(R_2-R_2')+\mathbf{x}_3(R_3-R_3') \ldots\}, \quad . \quad (12)$$

where $\mathbf{x}_1$, $\mathbf{x}_2$, $\mathbf{x}_3$ . . . are the components of the vector $\mathbf{x}$ distinguishing the various axes. $V\mathbf{fx}$ is then the determinant:

$$\frac{1}{2}\begin{vmatrix} 1 & 1 & 1 \\ \mathbf{x}_1 & \mathbf{x}_2 & \mathbf{x}_3 \\ (R_1+R_1') & (R_2+R_2') & (R_3+R_3') \end{vmatrix} \quad . \quad . \quad (13)$$

We may, however, immediately simplify these expressions by assuming for the present that the precessional rotation of which $\mathbf{x}$ is the unit vector is normal to the equatorial plane. If, then, $\mathbf{x}_2$, $\mathbf{x}_3$ . . . are regarded as situated in this plane, (12) reduces simply to $\frac{1}{2}\mathbf{x}(R_1-R_1')$, and (13) to

$$\tfrac{1}{2}\{(R_2+R_2')-(R_3+R_3')\}\mathbf{x}. \quad . \quad . \quad . \qquad (14)$$

It is to be noted that we are only justified in regarding R and R′ as conjugated in the manner shown, on the basis of our fundamental assumption that $\mathbf{p}=\mathbf{p}'$; *i.e.*, that the precessional rotations bring the moment of momentum into equilibrium. R and R′ may be regarded as belonging to different atoms of the molecule, or they may refer to orbits of the same atom. In the one case the equatorial plane will be placed at right angles to the "bond"; in the other it must lie in the atomic nucleus. For an atom, the effective atomic charge and the principal quantum number must be constant in both terms; in the molecule, however, both the atomic charge and the principal quantum number may vary. Introducing these expressions into equations (8) and (9), we shall have

$$\frac{\partial\mu}{\partial H}=-\frac{e^2}{4m^2c^2}\cdot\frac{m}{2}\left(\frac{3h^2}{8\pi^2me^2}\right)^2\left\{\frac{R_1}{Z^2}-\frac{R_1'}{Z'^2}\right\}\mathbf{yx} \quad . \qquad (15)$$

and

$$\frac{\mu}{H}=\frac{e^2}{4m^2c^2}\cdot\frac{m}{2}\left(\frac{3h^2}{8\pi^2me^2}\right)^2\left\{\frac{R_2-R_3}{Z^2}+\frac{R_2'-R_3'}{Z'^2}\right\}\mathbf{yx}. \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

The constant term becomes, on substitution of the appropriate values of the constants and multiplying by Avogadro's number,

$$D=\frac{9\times(6{\cdot}55\,.\,10^{-27})^4\times({\cdot}606\,.\,10^{24})}{512\times(3{\cdot}142)^4\times({\cdot}899.10^{-27})^3\times(1{\cdot}591.10^{-20})^2\times(3.10^{10})^2}$$
$$=1{\cdot}350\,.\,10^{-6}.$$

Introducing the values of R defined by the quantum factor of (11), we have finally for the expression of the diamagnetism χ_d,

$$\chi_d=-D\left\{\frac{n_1^2(n_1^2-k_1^2)}{Z^2}-\frac{n_1'^2(n_1'^2-k_1'^2)}{Z'^2}\right\}\mathbf{yx}, \quad . \qquad (17)$$

while the paramagnetism χ_p becomes

$$\chi_p=D\left\{\frac{n_2^2(n_2^2-k_2^2)-n_3^2(n_3^2-k_3^2)}{Z^2}\right.$$
$$\left.+\frac{n_2'^2(n_2'^2-k_2'^2)-n_3'^2(n_3'^2-k_3'^2)}{Z'^2}\right\}\mathbf{yx}. \quad . \qquad (18)$$

The factor **yx** represents the cosine of the angle made by the directions of the field and the magnetic moment. This we calculate from simple probability considerations. If there is only one direction in the molecule in which there is a magnetic moment (paramagnetic body) or in which a moment can be induced (diamagnetic), the average inclination will be given by $\cos^2\theta=\frac{1}{3}$, as in the well-known Langevin formula; if there are two such directions this factor will become $\frac{1}{2}$, while for three or more axes, which, of course, can all be resolved about three principal axes, simply 1. We thus put in the three cases $\cos\theta=1/\sqrt{3}$, $1/\sqrt{2}$, and 1 respectively. In the case of a paramagnetic substance, Sommerfeld ('Atomic Structure,' Eng. trans. p. 250) has suggested quantizing these angles in terms of the possible values which can be adopted by the azimuthal quantum number of the orbits. On the present theory all values which can be adopted by the equatorial and latitudinal quantum numbers are not admissible, so the method must be rejected.

In order to test these equations, we may first consider diamagnetic molecules which can be regarded as dipoles. It will then be necessary to make some consistent assumption as to the effective atomic numbers. If we regard the molecule as linked by a single bond in the chemical sense, or if we have to deal with an atom which has a single electron in the valency shell, we assume that the effective atomic number is unity. In the case of the metals in the first group of the periodic table, this assumption will be readily conceded; with such effectively monovalent elements as the halogens, our assumption depends on the electronic constitution we assign to the shell below the valency shell. As we shall have to refer repeatedly to this shell, it will be a convenience to number our shells from the outside inwards, instead of by the commonly adopted spectroscopic convention of numbering them from the nucleus outwards. If we call the valency shell V, let us call the one below W. It will probably not be necessary to go deeper into the constitution of the atom. In a halogen molecule, as already explained, we assume a joint W shell. For chlorine and elements of higher atomic number this shell is composed of two groups of six electrons each. Fluorine is not able to assume this configuration, as its X shell, which is the same as that usually designated K, would then only contain two electrons; the shell of eight electrons, which must intervene between a K ring and an M shell containing groups of six, would be absent. Fluorine will be anomalous in this respect therefore, in that it cannot be regarded as effectively monovalent like the other halogens. This fixing of the effective atomic number is, of course, purely arbitrary, and can only be justified by results. The mechanism by which this change comes about, and which may eventually afford a quantitative account of the process, appears reasonably clear. On combination of two atoms, our fundamental postulate states that the energy represented by the difference of the two terms representing the natural frequency of the valency electrons of the uncombined atoms becomes "available." Part of this energy goes to alter the kinetic energy of the electrons so that their frequencies are synchronized; part is absorbed in the molecular structure as potential energy, and the excess or deficit becomes "free" and represents the heat of the reaction. Although not at present mathematically demonstrable, we assume that this potential energy is responsible for changing the effective atomic numbers of the molecule. The ratios of the kinetic and potential energies in the magnetic field we have calculated (*loc. cit.*). In the magnetic field it was shown that

$$E_{\text{kin}} = -\tfrac{3}{2}E_{\text{pot}}. \qquad (19)$$

This relation has made possible the calculation of heats of reaction of simple substances by using as effective atomic numbers for the uncombined atoms those which result by subtracting the Sommerfeld screening number corresponding to the number of free valency electrons from the number which locates the element in the appropriate vertical column of the periodic table. For the purposes of calculating the magnetic properties, we here assume the molecular effective atomic number; an atom will still retain the effective atomic number calculated as before. A difficulty arises in the case of a rare gas, or an atom, significantly for example iron, which has a complete quantum group for its V shell. According to its position in the periodic table the effective atomic number of such atoms should be zero, which would make the para- or diamagnetism infinite. The actual number must therefore be small. It will be seen in what follows that the very high dia-magnetism of the rare gases, and the exceptional para-magnetism of iron, can be explained on this hypothesis, and an empirical number found which will account quantitatively for the observed results.

The precessional rotations which respond to the imposed magnetic field in diamagnetic atoms are those which depend on the asymmetry of the *k* numbers of the orbits. In a polar molecule, as has been emphasized in the well-known octet theory of Lewis and Langmuir, each ion attains a rare gas V shell by exchange of electrons; this same hypothesis was used in calculating the heats of formation of polar molecules. The diamagnetism of such compounds should then be calculated as the sum of the individual values of the ions which are regarded as atoms with eight valency electrons, but with atomic numbers of +1 and −1 respectively. As the effective atomic number enters as the square, Z^2 is 1 in both cases. Equation (17) then shows that diamagnetism will be given by

$$\chi_d = -D\{[n_1^2(n_1^2-k_1^2)-n_1^2(n_1^2-k_1'^2)] + [n_2^2(n_2^2-k_2^2)-n_2^2(n_2^2-k_2'^2)]\}\cos\theta. \quad . \quad (20)$$

Here the numerical suffixes 1 and 2 refer to the different *ions* and not to the axis concerned. For each ion the principal quantum numbers n_1 and n_2 are constant. The paramagnetism according to equation (16) must obviously be zero. The expression then simply reduces to

$$\chi_d = -D\{n_1^2(k_1'^2-k_1^2)+n_2^2(k_2'^2-k_2^2)\}\cos\theta.$$

The pairs of electrons belonging to each atom must have different values of k and k'. By the hypothesis of exchanges of half quantum numbers with the nucleus or trunk, in the manner Sommerfeld and Pauli have employed in calculating the anomalous Zeeman effect, an azimuthal quantum number of 2 becomes 3/2 and one of 1 becomes 1/2. This hypothesis is employed consistently in all that follows.

Since $(k_1'^2-k_1^2)=(k_2'^2-k_2^2)=(9/4-1/4)$, and $\cos\theta$ must be $\sqrt{1/3}$, we shall have simply

$$\chi_d = -\frac{2D}{\sqrt{3}}(n_1^2+n_2^2). \quad . \quad . \quad . \quad . \quad (21)$$

Table I. gives the results obtained by calculating on the above formula the values of the diamagnetism for the compounds shown. The experimental results are taken from Landolt and Börnstein (1921 edition). The values χ_M used are the arithmetical means of the observed values multiplied by the molecular weight. In the divalent compounds, simply twice the value for the halogen ion has to be taken in the theoretical formula. It will be seen that in the case of the alkali metals and alkaline earths the agreement is as good as can be expected when the inaccuracy of the experimental results is considered. The fluorides are, however, distinctly abnormal, as was to be expected and as has been consistently observed in previous work. The experimental results are not sufficiently reliable to warrant

TABLE I.

Polar Compounds.

	$\chi_m \times 10^6$.	$\chi_M \times 10^6$.	n_1.	n_2.	$\frac{(n_1^2+n_2^2)\times 2{\cdot}70}{\sqrt{3}}$.
NaCl ……	−0·41, −0·58	−29·0	3	3	−28·0
NaBr ……	−0·37	−38·1	3	4	−38·9
NaI ………	−0·31, −0·45	−57·0	3	5	−53·0
KCl ………	−0·47, −0·55 −0·45	−36·5	4	3	−39·0
KBr………	−0·35, −0·45	−47·6	4	4	−49·9
KI ………	−0·31, −0·45	−63·1	4	5	−63·9
LiCl………	−0·46	−19·5	1	3	−20·26
$MgCl_2$ ……	−·50, −0·46, −·45	−44·6	3	3	−42·1
$CaCl_2$ ……	−·43, − ·41, −·43	−46·6	4	3	−53·0
$SrCl_2$ ……	−·44, − ·40	−66·2	5	3	−67·0
$SrBr_2$ ……	−·31	−76·8	5	4	−88·8
SrI_2 ………	−·35	−119·4	5	5	−117·0
$BaCl_2$ ……	−·32, − ·41, −·32	−72·6	6	3	−84·2
$BaBr_2$ ……	−·31, − ·41	−107·1	6	4	−106·0
BaI_2 ……	−·41, − ·30	−140·8	6	5	−134·0
NaF ……	−·40	−16·82	3	2	−20·2
KF ………	−·45	−23·2	4	2	−31·2
CaF_2 ……	−·30	−17·4	4	2	−37·4
SrF_2 ……	−·26	−27·4	5	2	−81·4
BaF_2 ……	−·13	−20·2	6	2	−68·6
$ZnCl_2$ ……	−·15	−68·2	4	3	−53·0
$HgCl_2$ ……	−·24	−66·4	6	3	−84·2
$HgBr_2$ ……	−·26	−93·8	6	4	−106·0
AgCl ……	−·28	−40·1	5	3	−53·0
AgBr ……	−·26	−48·9	5	4	−63·9
AgI ………	−·29	−68·1	5	5	−77·9

attempting to discover the appropriate relation. We may require to adopt a different effective atomic number for the fluorine ion, or the ion may become paramagnetic. The results for the base and noble metals are similarly not so good as the other results. Silver appears uniformly high, as also do zinc and mercury. Here, again, the effective atomic number for atoms whose V shell is composed of three groups of six electrons may be greater than that for the usual eight.

The same method of calculating should enable us to arrive at the diamagnetism of the halogen elements. Here we assume, as we have done consistently in calculating the energy relations, that one of the atoms contains an activated orbit. The effective atomic number is constant in both terms. The molecular diamagnetism should then be calculated precisely as above except that n_2 is equal to n_1+1. Since only one valency orbit is activated, the remaining orbits in both atoms will be symmetrical, and there will therefore be no paramagnetism. The values so obtained are shown below.

TABLE II.

	$-\chi_m\times10^6$.	n_1.	n_2.	$-\chi_d$ calc. $\frac{2Dn^2+(n+1)^2}{\sqrt{3}}$.	$-\chi_M$ found.
Cl......	0·59	3	4	39·9	42·2
Br ...	0·21, 0·38, 0·40 0·403	4	5	63·9	60·0
I	0·39, 0·36, 0·35 0·40, 0·30, 0·37	5	6	95·1	99·0

Hydrogen should be calculable on our hypothesis that one atom becomes activated. We assume that the molecular azimuthal quantum number for this atom is 3/2. This will be readily accepted, as obviously the moment of momentum of the activated atom must decrease. The susceptibility will then be given by

$$\chi_M = -D\,\frac{4(4-9/4)-1(1-1/4)}{\sqrt{3}} = -{\cdot}4{\cdot}87\times10^{-6}.$$

The value found by Také Soné for $-\chi$ is 1·982 for the atom or 3·995 for the molecule. Kammerling Onnes, however, arrives at the value 2·7 for the atom or 5·4 for the molecule. This latter value is quoted by Pascal (*Comptes Rendus*, clvi. p. 324, 1913) in support of a value of 2·93, which represents the average value for the increase in the diamagnetism in saturated hydrocarbons. The mean of Také Soné's and Onnes' values is nearly 4·7. A discrepancy of this magnitude would not be surprising, considering the difficulty of the experimental measurements. As regards the value for the diamagnetism of hydrogen in combination, it is extremely doubtful that this should have the same value as in molecular hydrogen. The following considerations afford a probable explanation of the reason for the approximate agreement noted by Pascal. For the diamagnetism of a

C—H bond on the present theory we should write

$$D\frac{4(4-9/4)-1(1-1/4)}{\sqrt{3}}=4\cdot87\times10^{-6};$$

i.e., the same value as for molecular hydrogen. For the C—C link we should have similarly

$$D\frac{4(4-9/4)-4(4-1/4)}{\sqrt{3}}=6\cdot236\times10^{-6}.$$

This is near the mean value given by Pascal (6·0).

On increasing the length of a chain in a saturated hydrocarbon, each additional carbon carries with it two hydrogens. The bonds by which they are attached cannot both possibly orientate themselves in the same direction as the external field. They will make an angle of 109° 28′ with one another. This angle, as has been pointed out in the previous paper, is a consequence of spatial quantizing; it represents the solid angles between four vectors, three of which make an angle whose cosine is 1/3 with the direction of the field, and which are arranged symmetrically about the axis, the fourth being parallel with the field in the negative direction. The average angle which each bond will make with the field is thus 50° 44′. 4·87 multiplied by the cosine of this angle is 2·82, which is reasonably near Pascal's average. The value for carbon will be correct, as each additional carbon only involves one extra C—C link. It is thus obvious that the additive constants extracted by Pascal do not represent the intrinsic susceptibilities of the atoms. These have to be multiplied by a probability factor; in fact, his constants do not give values for the *atom*, but rather for the bonds which that atom can form with other elements, a consideration which makes it obvious that spatial probabilities must be considered. The very valuable data which Pascal has compiled are, however, likely to be of great value in extending, along the lines developed here, our knowledge of molecular structure. The examination of this aspect of the subject is reserved for another communication. At present it will be advisable to take a general survey of the applicability of the theory.

Nitrogen calculated by the simple addition formula should have a susceptibility of

$$\frac{(4+9)\,D}{\sqrt{3}}=10\cdot13\times10^{-6}.$$

The value given by Také Soné is 7·42. There is no doubt, however, that we should be incorrect in calculating nitrogen as a simple monovalent compound. Since there are now three free valencies to each atom according to the scheme $\overset{\cdot\;\;\cdot\;\;\cdot}{\underset{\cdot\;\;\cdot\;\;\cdot}{2\,(\overset{\frown}{2\cdot2})\,2}}$, we are not justified in neglecting the operators Ω_2 and Ω_3 of equation (12). Our formula should then be

$$\chi_d = -\frac{D}{Z^2}\{\Omega_1\mathbf{x}_1 + \Omega_2\mathbf{x}_2 + \Omega_3\mathbf{x}_3\}\mathbf{y}\,. \quad . \quad . \quad . \quad (22)$$

The two electrons of like azithmuthal quantum numbers of each atom will arrange themselves symmetrically in the equatorial plane; it is thus clear since $R_2 = R_3$, $R_2' = R_3'$ that the molecule cannot be paramagnetic. Of the R_1 and R_1' bonds, one must be derived from an excited orbit. Equation (22) thus becomes

$$\chi_m = -\frac{D}{Z^2}\left\{\left[9\left(9-\frac{9}{4}\right)-4\left(4-\frac{1}{4}\right)\right]\mathbf{x}_1 + 8\mathbf{x}_2 + 8\mathbf{x}_3\right\}\mathbf{y}. \quad (23)$$

We now have to consider the probabilities for the cosines $\mathbf{x}_1\mathbf{y}$, $\mathbf{x}_2\mathbf{y}$, and $\mathbf{x}_3\mathbf{y}$. If $\mathbf{x}_1$, $\mathbf{x}_2$, and $\mathbf{x}_3$ are at right angles, our probable angle will be cos 1. For an atom with three valency electrons the effective atomic number will be $3 - {\cdot}577 = 2{\cdot}423$, where $0{\cdot}577$ is the Sommerfeld screening number for three electrons. Z^2 should thus be $5{\cdot}867$. The above factors should then give $14{\cdot}2 \times 10^{-6}$. Také Soné's value expressed for the molecule is $14{\cdot}82 \times 10^{-6}$.

Experimental results for solid compounds are well known to be liable to very considerable errors. It will be interesting to compare a few results for elements where experimental values can be relied on with a fair amount of accuracy. An *element* (atom) with an odd number of valency orbits should always be paramagnetic unless a diatomic molecule is formed. While the alkalies and alkaline earths are uniformly paramagnetic, the metals in the sub-groups of the first two columns of the periodic table are diamagnetic. This must mean either that they form diatomic molecules, or that the V electrons can lock up with one of the groups of six in the W shell to form a system of zero moment. Only elements which can exist in more than one stage of "oxidation" in the chemical sense would be expected to show this property. There are thus alternative methods of calculating the diamagnetism of these elements:—

(1) As monatomic "rare gas" atoms with the appropriate atomic number and $\cos\theta = 1$. χ_M will then be given by

$$\chi_d = -\frac{D}{Z^2}\left\{n^2\left(n^2-\frac{1}{4}\right)-n^2\left(n^2-\frac{9}{4}\right)\right\} = -2\frac{Dn^2}{Z^2}. \quad . \quad (24)$$

The principal quantum number does not change. The value of χ_d so obtained will be that of an atom.

(2) As non-polar combinations similar to hydrogen. Here the principal quantum numbers differ by unity due to excitation of one orbit; $\cos\theta$ will be determined by the number of axes about which precession can occur as explained before. If there are three such axes as in the the case of nitrogen, $\cos\theta$ will be 1.

Table III. gives the results for various elements calculated according to these methods. The experimental values of χ_m, found in Landolt and Börnstein, are given in column 1. In column 2 are the limiting values deduced by Pascal (*loc. cit.*) from the additive relations in organo-metallic compounds. Column 8 gives the theoretical results calculated on the simple monatomic formula (24). Column 13 gives the results calculated according to formula (22). The equatorial components R_2, R_3 are shown in columns 10 and 11.

Silver and gold, as might be expected, appear to be diatomic. Zinc, cadmium, and mercury show reasonable agreement when calculated as monatomic atoms. The two free valency electrons appear to lock up with a six of the W shell; $\cos\theta$ must then be equal to 1. Nitrogen and boron both having three free electrons should be calculated by the same formula. Both give values for the susceptibility which, calculated as a molecule, is near that observed. Phosphorus, arsenic, and antimony appear to tend to become monatomic. This must be connected with the fact that after phosphorus a group of six electrons can be formed. Possibly two electrons go to one atom, forming with a six an eight ring, and six remain on the other. They would then behave like ordinary polar molecules, as the formula used would indicate. For the other elements, the experimental results are too variable to allow of any useful comparisons being made. Unfortunately the condition of spatial quantizing vitiates the results obtained by Pascal, as pointed out in the case of the carbon hydrogen link. Enough has been shown, however, to give confidence in the general applicability of the formulæ.

TABLE III.

				MONATOMIC.				DIATOMIC.				
	$-\chi_m \times 10^6$. (Observed.)	$-\chi_M \times 10^6$.	$-\chi_M \times 10^6$. (Pascal.)	n.	Z^2.	$\cos\theta$.	$-\frac{2Dn^2}{Z^2}\cos\theta$.	Z^2.	R_2.	R_3.	$\cos\theta$.	$-\chi_d = \frac{D}{Z^2}(R_1+R_2+R_3)\cos\theta \times 10^6$.
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
Ag......	·19, ·22, ·20, ·187	21·6	...	5	...	...	......	1	0	0	$\sqrt{1/3}$	38·97
Au ...	·141, ·15	28·8	...	6	...	...	......	1	0	0	$\sqrt{1/3}$	56·10
Zn	·15, ·15, ·10, ·10	9·87	...	4	3·061	1	10·44					
Ca	·17, ·15, ·179	19·3	...	5	3·061	1	22·05					
Hg	·19, ·19, ·18	31·2	...	6	3·061	1	31·75					
N	·265 (T. S.)	7·42	...	2	1	...	......	5·865	$2n^2$	$2n^2$	1	14·2
B	·71, ·8, ·66	7·6	...	2	1	...	......	,,	,,	,,	,,	,,
P	·869, ·88, ·92 ·73 (·23)	11·3	...	3	1	$\sqrt{1/3}$	14·0	,,	,,	,,	$\sqrt{1/3}$	23·6
As	·3, ·30	22·3	...	4	1	$\sqrt{1/3}$	24·9	,,	,,	,,	,,	46·4
Sb	·57, ·94, ·815	37·0	...	5	1	$\sqrt{1/3}$	38·9	,,	,,	,,	,,	85·9
C	......	...	6·0	2	1	$\sqrt{1/3}$	6·23					
S	·34, ·485, ·51 ·48, ·49	15	15·0	3	1	$\sqrt{1/3}$	14·0					

The rare gases are of great interest. The value χ_m for argon, as found by Také Soné, is the enormous magnitude of about -236×10^{-6}. Helium, according to Tänzler (*Ann. de Phys.* (4) xxiv. p. 931, 1907), must be in the neighbourhood of $44{\cdot}8\times10^{-6}$. Calculated as rare gases from the observed susceptibilities, the Z's should be given by

$$Z\ (\mathrm{He})=\frac{2{\cdot}7}{44{\cdot}8}={\cdot}06$$

and

$$Z\ (\mathrm{A})=\frac{2{\cdot}7\times9}{236}={\cdot}105.$$

The mean of these values for the effective atomic number of a rare gas is in the neighbourhood of $\frac{1}{16}$; with which speculative number we can test the theory by applying it to a paramagnetic atom with a "rare gas" valency shell.

One further example of the calculation of diamagnetism may be given. The susceptibility of water, calculated as a non-polar molecule, should be given by

$$\chi=\frac{2\{4(4-\frac{9}{4})-1(1-\frac{1}{4})\}\mathrm{D}}{\sqrt{2}}=-11{\cdot}93\times10^{-6}.$$

The experimental value is between $-12{\cdot}58$ and $-12{\cdot}94\times10^{-6}$, the value decreasing as the temperature is lowered.

In order to calculate the paramagnetism in a manner which will enable comparison with experimental results, it will be necessary to derive an expression which will be independent of the applied field and the temperature. We must then substitute for the internal field H of equation (16) in terms of the precessional velocity.

If we are dealing with a molecule, our fundamental hypothesis states that q will be related with the available energy derived by the accommodation of the natural frequencies of the uncombined atoms.

This energy,

$$\mathrm{E}_a=\Delta\mathrm{E}_{\mathrm{kin}}+\Delta\mathrm{E}_{\mathrm{pot}},$$

will be distributed in the molecule in such a way that the relation developed for the ratios of kinetic and potential energy in the magnetic field holds. This relation, already referred to, is

$$\Delta\mathrm{E}_{\mathrm{kin}}=-\tfrac{3}{2}\Delta\mathrm{E}_{\mathrm{pot}};$$

so we may write

$$\Delta\mathrm{E}_{\mathrm{kin}}=3\mathrm{E}_a. \qquad (25)$$

The relation between the change in the kinetic energy of an electronic orbit and an external field involves, in Sommerfeld's notation, the latitudinal quantum number n_1, which defines the moment of momentum $p_\psi = \int p_\psi d\psi = n_1 h$, where the angular coordinate measures the longitude in the rotating system of reference. This quantum number we will refer to as l, in order to distinguish it from the other n's. $\frac{1}{k}$ is thus the cosine of the angle made by the vector normal to the orbit and the direction of the field.

$\triangle E_{\mathrm{kin}}$ can then be shown to be equal to

$$\frac{lOh}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (26)$$

The available energy of accommodation E_a is given by $hR_0\left(\frac{Z^2}{n^2} - \frac{Z'^2}{n'^2}\right)$, where R_0 is the Rydberg constant. In virtue of (26) and (25) we then have

$$O = q = \frac{2\pi}{lh} \triangle E_{\mathrm{kin}} = \frac{6\pi}{l} R_0 \left(\frac{Z^2}{n^2} - \frac{Z'^2}{n'^2}\right).$$

We assume that 1 is the smallest value the latitudinal quantum number can assume. The justification for this assumption may be sought in the hypothesis that the energy is distributed in such a way that the largest possible amount of energy appears in kinetic form. As we admit of half quantum numbers in the molecule, replacing 1 by the value 1/2 and substituting in (7), we have

$$H = 24 \frac{\pi mc}{e} R_0 \left(\frac{Z^2}{n^2} - \frac{Z'^2}{n'^2}\right). \quad . \quad . \quad . \quad . \qquad (27)$$

Substituting this in (10), we then have

$$\mu = \frac{27}{16} \frac{ehL}{4\pi mc} \left(\frac{Z^2}{n^2} - \frac{Z'^2}{n'^2}\right)\left(\frac{R_2 - R_3}{Z^2} + \frac{R'_2 - R'_3}{Z'^2}\right) \cos\theta.$$

The factor $\frac{ehL}{4\pi mc}$ is the gram-molecular unit of magnetic moment or Bohr, and is equal to 5584 gauss × cm.; so the formula may be written simply

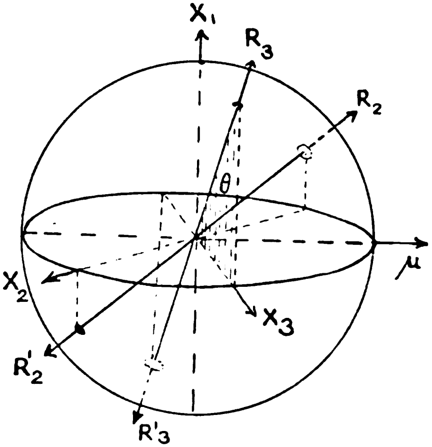
$$\mu = \frac{27}{16} B \left(\frac{Z^2}{n^2} \quad \frac{Z'^2}{n'^2}\right)\left(\frac{R_2 - R_3}{Z^2} + \frac{R_2' - R_3'}{Z'^2}\right) \cos\theta. \qquad (28)$$

The values of μ so calculated should give the values of the magnetic moment as calculated by the Langevin formula $\mu = \sqrt{\frac{CR}{\overline{\cos^2}\theta}}$, where C is the Curie constant and R the gas constant for the gram molecule, and $\overline{\cos^2}\theta = 1/3$. The results may first be tested with the paramagnetic gases oxygen and nitric oxide.

We suppose that oxygen has two electrons belonging to each atom which remain free, the remaining eight locking up together as a W shell.

Fig. 1 represents the disposition which is assumed. The angle θ represents the inclination of the vector normal to the orbits with the direction of μ, which, according to (10), must lie in the equatorial plane. Cos θ now has a different meaning from that which it has in the expression for diamagnetism, as can be seen by referring to our development of equations (13) and (14). The angle θ in this case we may fix by spatial quantizing, as was done by Sommerfeld. Since we are dealing with $k = 3/2$ orbits, the admissible angles will be $\cos\theta = 1/3$, $2/3$, and 1, whence the average angle is given by

Fig. 1.



$$\overline{\cos}\,\theta = \sqrt{\frac{1}{3}\left(\frac{1}{9}+\frac{4}{9}+1\right)} = \sqrt{\frac{14}{27}}.$$

The probability angle, which the direction of the moment μ will make with the direction of the external field, is accounted for by the factor $\sqrt{3}$ in the Langevin formula.

In comparing results with the magneton numbers determined by Weiss and others, we therefore do not have to take it into account.

Substituting the appropriate values in (28), we thus have

$$\mu = \frac{27}{16} \mathrm{B} \left\{ \left(\frac{1}{9} - \frac{1}{4} \right) \left[4 \left(\frac{9}{4} - \frac{1}{4} \right) + 4 \left(\frac{9}{4} - \frac{1}{4} \right) \right] \right\} \cdot \sqrt{\frac{14}{27}}$$

$$= 2{\cdot}699 \text{ B}.$$

This figure multiplied by 5 will give the result in Weiss magnetons. We thus compare an entirely theoretical value of 13·5 with values of 13·9 and 14·2 determined by Weiss and quoted by Sommerfeld (*C. R.* clv. p. 1234, 1912 and clvii. p. 916, 1913; *Journ. de Phys.* p. 97, 1920). Our value multiplied by 5 is 13·2. The approximation of the result is satisfactory, especially as the method by which it was derived involved the hypothesis which distributes the available energy of accommodation in the molecule. It may be noted, however, that the frequency term includes a quantum number 3; *i. e.*, it refers to an activated oxygen orbit, whereas the inertial terms depend only on the unactivated principal quantum number. This does not appear an objection; it simply means that on re-distribution of energy the orbit once more assumes the value it has in its ground orbit.

Nitric oxide, which has only one free bond, should simply be half the value for oxygen with the $\sqrt{\frac{14}{27}}$ omitted. This gives 15/8 B or 9·38 Weiss. The value found is 9·2. This assumes, of course, that the accommodation energy is derived from the same element which has the free bond, otherwise the Z's would not cancel. These results, although only approximate, at least afford considerable support to the theory in its qualitative aspects. It is quite clear that under no circumstances can these molecules be other than paramagnetic.

The author takes this opportunity of expressing his indebtedness to Dr. J. W. Nicholson and Dr. N. V. Sidgwick for the interest they have shown in this and preceding papers, and to Mr. T. W. J. Taylor for the trouble he has taken in correcting proofs.

Irrigation Research Department,
Punjab University Chemical Laboratories,
Lahore, November 1924.

CXV. *A Note on the Photo-activation of Chlorine.* *By* WILFRID TAYLOR, *B.Sc., Research Scholar Armstrong College, Newcastle-on-Tyne*[*].

THE increased chemical activity of chlorine under the influence of visible light has received much attention owing to the various photo-chemical reactions to which it gives rise, notably the synthesis of hydrogen chloride. Many attempts have been made to trace an antecedent physical change in the chlorine: Kummel and Wobig have shown that there is no dissociation[†], J. J. Thomson, Lenard, and others that there is no ionization[‡], Bovie[§] and Wendt[||] that the activity ceases immediately on cutting off the light, while Mellor[¶] explained the Budde effect[**] as a heating due to the reaction of the chlorine with water vapour. As a plausible assumption it may therefore be supposed that the chlorine molecule absorbs energy from the radiation (or from the secondary radiation as suggested by Weigert[††]) and thereby undergoes a change of internal configuration, passing to a state of greater energy corresponding to an increase in the electronic and vibratory quantum numbers. The new state may be termed "activated," and would be characterized by a weakening of the chemical bonds, as suggested by J. J. Thomson[‡‡] and recently deduced from spectroscopic considerations by V. Henri in the cases of naphthalene[§§] and sulphur[||||].

The initial configuration of the molecule is governed by the quantum equation

$$E_n = \oint p\, dq = nh,$$

and the absorption obeys Bohr's frequency condition

$$h\nu = \delta E = E_m - E_n.$$

Hence no incident light can have any effect unless its frequency ν is at least sufficient to furnish the necessary quota δE. If the final state E_m is not quantified, ν will then be a threshold value above which light is absorbed, and in the presence of a suitable reagent chemical action commences.

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[*] Communicated by Prof. G. W. Todd, M.A., D.Sc.

[†] Kummel and Wobig, *Zeit. fur Elektrochemie*, xv. p. 252.

[‡] J. J. Thomson, Proc. Camb. Phil. Soc. xi. p. 90 (1901).

[§] Bovie, Journ. Amer. Chem. Soc. xxxvii. p. 1721.

[||] Wendt, Journ. Amer. Chem. Soc. xliv. p. 2377.

[¶] J. W. Mellor, Trans. Chem. Soc. lxxxi. p. 1280 (1902).

[**] Richardson, Phil. Mag. xxxii. p. 227 (1891).

[††] F. Weigert, *Zeit. Physikal. Chem.* cvi. p. 407 (1923).

[‡‡] J. J. Thomson, "The Electron in Chemistry."

[§§] V. Henri and De Laszlo, Proc. Roy. Soc. 105 A, p. 662 (1924).

[||||] V. Henri and Teves, 'Nature,' cxiv. p. 994 (Dec. 1924).

It becomes of interest, therefore, to investigate the relation between the activation, and the frequency of the illumination; quantitative work in this direction does not appear to have been published, and only recently has a similar investigation been made on the photo-dissociation of sulphur dioxide*. In the present work the photo-synthesis of HCl was used as the criterion of the activation of the chlorine, and the reaction velocity determined for different parts of the spectrum.

A modified form of the actinometer used by Burgess and Chapman † was employed. It consisted essentially of a bulb in which the gas mixture was illuminated, and having a layer of water in the lower portion to absorb any HCl formed. By means of stopcocks, it could be placed in communication either with an exit tube, or a narrow bore calibrated index tube. Any contraction in the gas volume was then measured by the movement of an indicator in the latter. The whole apparatus was made of glass, and immersed in a large water-bath to ensure temperature stability, an air thermometer being placed beside the bulb as a further check. The bath was encased in an opaque cover provided with a small window.

The gases were provided by the electrolysis of pure concentrated HCl with a current of 2 amps. and the cell used at the point of minimum oxygen adulteration according to Chapman ‡. The cell was run for 40 hours to saturate all the liquid and expel atmospheric air. To decrease the effect of inhibiting agents, the incoming gases were passed through a suitably adjusted beam of white light. A very sensitive gas mixture was finally obtained.

The illumination was provided by a "Pointolite" electric arc which had the advantage of a very low percentage of accompanying heat radiation; the point source enabled the light to be brought to a focus by a lens system. This focus fell in the plane of an aperture fitted with a shutter, and having a water-cell and light filter behind the latter. The colour filters made by the Ilford Company were used, and by their means, narrow bands could be isolated from the continuous spectrum, of approximately equal width, and without any extraneous radiation whatever. After diverging from the focus, the rays passed through the window of the water-bath and fell upon a gas bulb.

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* R. A. Hall, Trans. Faraday Soc. xx. p. 107 (1924).

† Burgess and Chapman, Journ. Chem. Soc. lxxxix. 2, p. 1399 (1906).

‡ Chapman and MacMahon, Journ. Chem. Soc. xcv. pp. 135 and 959.

In making an exposure, the water in the bulb was tested for complete chlorine saturation, and the bulb filled by allowing the gas mixture to pass through it for half an hour. All taps were then closed, and the apparatus left for half an hour in the dark to test equilibrium. The shutter was then opened, and timed readings of the indicator taken. The period of inertness was always observed, followed by the growth of the reaction velocity to a steady rate. With the most sensitive mixtures, a large Draper effect was noticed. The chief source of difficulty was found to be the retarding of the reaction by inhibiting agents present in minute quantity. A series of exposures under apparently identical conditions gave readings which varied by as much as 200 per cent. This negative catalysis has been studied by Burgess and Chapman * and the latter has also shown theoretically that the retardation is proportional to the quantity of inhibitor present †. Precautions were therefore taken of running strongly illuminated chlorine through the apparatus for a long period, and carefully standardizing the filling operations. Reaction velocities for the same conditions could then be repeated within 1 per cent. Each exposure was accompanied by a standard "control" exposure. The time-contraction readings being plotted for each light filter, the straight portions of the graphs gave by their gradients constants measuring the corresponding reaction velocities, and hence the activation of the chlorine. The limits of the spectrum bands were measured by a spectrometer; the extreme edges are given below, but margins within these limits would be ineffective owing to relative faintness. Eight filters were used covering the whole visible spectrum, but only three produced any measurable effects. With the green filter, no movement of the index could be observed over a long exposure with a pre-sensitized mixture which responded instantly to the blue-green.

The figures thus obtained do not, however, take into account the possibility that the filters might not transmit the same amounts of radiant energy. If we assume that for the same frequency the activation is proportional to the energy in the beam, then a correction could be made by reducing these reaction velocities to equivalent illumination intensities. A thermopile was therefore substituted for the bulb, and

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* *Loc. cit.*

† *Loc. cit.*

connected in series with a Kelvin mirror galvanometer; as a first approximation, the steady deflexions were taken as measures of the intensities, and used as correction factors.

Filter.	Reaction velocity.	Range of wave-band (Angström units).	Relative light intensity.	Corrected Activated power.
Violet	100	4300–4800	7	100
Blue	27	4550–5000	11	17
Blue-green ...	14	4780–5370	13	8
Green	0	5050–5570	15	0

The activating region of the spectrum therefore corresponds to that of the general absorption of chlorine itself, *i. e.* with the continuous band extending from about 4900 A.U. at normal temperature * and pressure † and not with the Riband fine structure bands. Activation would therefore seem in this case to be concomitant with the non-quantification of the vibratory motions.

In conclusion, I should like to express my indebtedness to the helpful criticism of Professor G. W. Todd throughout the course of this work.

CXVI. *Constancy of Total Photo-Current from Sodium with Temperature Change* 20° *C. to* −190° *C.*‡ *By* Robert C. Burt §.

In order to obtain uncontaminated sodium surfaces, the cells used in this experiment were prepared by driving sodium electrolytically through the walls of a highly evacuated bulb ‖. Much light has been thrown upon the mechanism of this remarkable phenomenon in a paper which Joffe ¶ has recently published. The method was brought to my own attention by Dr. A. W. Hull, whose kindness in performing for me such an electrolysis in his laboratory I am pleased to acknowledge. It is appropriate to describe it as electrolysis through glass.

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* Dobbie and Fox, Proc. Roy. Soc. 99 A, p. 456.

† Narrayan and Gunnaya, Phil. Mag. xlv. p. 830.

‡ Dr. H. E. Ives, Jour. of Optical Soc. of America, vol. viii. No. 4, p. 551.

§ Communicated by Prof. R. A. Millikan.

‖ E. Warburg, *Wied. Ann.* xxi. p. 622 (1884); id., *ibid.* xl. p. 1 (1890). A. Herz, *ibid.* liv. p. 245 (1895). W. P. Graham, *ibid.* lxiv. p. 51 (1898). C. A. Skinner, *ibid.* lxxviii. p. 754 (1899). K. Mey, *Ann. der Phys.* (4) xi. p. 130 (1903). W. Neuswanger, Phys. Rev. (2) vii. p. 263 (1916). For complete bibliography, see "The Electrical Conductivity of Sodium Chloride in Molten Glass" by Willard J. Sutton and Alexander Silverman, Journal of the American Ceramic Society, vol. vii. No. 2, February 1924, p. 102.

¶ A. Joffe, *Ann. der Physik,* lxxii. p. 461.

The arrangement used in these experiments was as follows. A 40 watt incandescent lamp bulb (the well evacuated tungsten filament lamp in most common use today) was immersed, stem up, in a molten salt or salt and water solution containing sodium ions, and a potential of about 100 volts was applied between the lighted filament and the solution surrounding the lower part of the bulb. The bulb itself is of soda glass—an essential condition. The vacuum, rendered conducting by electrons from the filament, is, so to speak, electroplated by the sodium which passes from the solution anode through the glass electrolyte.

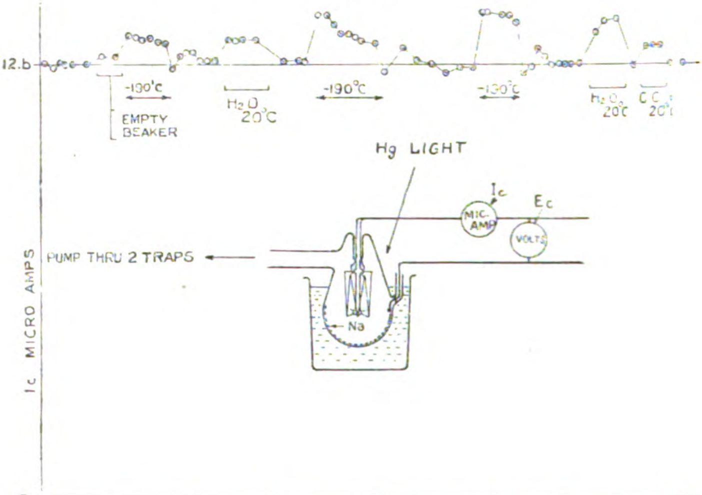
Since a larger electrolytic current can be sent through the glass if it is hot, I have used in place of a water solution molten sodium nitrate, which melts at 312° C. This is well below the baking-out temperature which had previously been maintained for more than 24 hours. At the temperature of 312° C. the sodium evaporates and condenses at the top-inside of the bulb above the level of the hot surrounding sodium nitrate. However, it can be redistilled into the bottom when it is once inside. The filament when not lighted is used as a collector for the photo-electrons. By keeping it heated during the redistillation no sodium can condense upon it. During redistillation the pressure of sodium vapour must not become too high else a sodium arc will form and burn out the filament. Currents as large as 0·2 ampere have been used for this electrolysis; larger currents are likely to burn out the filament. Control of the electrolytic current is obtained by adjusting the temperature of the filament.

It was found that the vacuum inside cells which had been sealed off the pumps was not sufficiently perfect to keep the sodium surface clean, even with the use of charcoal side tubes. For this reason the results reported here were obtained with cells which were attached to the mercury pumps, although results similar to those given here on contaminated surfaces were obtained in cells which had been sealed off.

In the centre of fig. 1 is shown the cell which is connected through two liquid-air traps to two diffusion pumps. Light is incident from above on the sodium surface at the bottom of the bulb. With a constant potential (measured by a Weston model 45 voltmeter) on the collector the total photocurrent is measured (by means of a Rawson unipivot milammeter, type 501) while the illumination is held constant.

At the top of fig. 1 have been plotted photo-currents against time. Under the influence of the light the photo-current was constant at 12·6 micro-amperes. But when the empty beaker was put in place about the cell there was a small increase in the current as shown, and when liquid air was put in the beaker there was a greater increase. The photo-current decreased as the liquid air evaporated. When the air was removed, the current returned to 12·6,

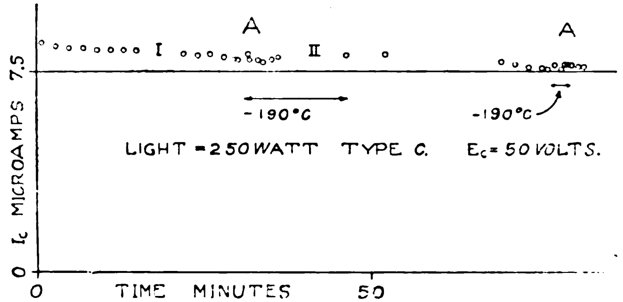
Fig. 1.



and when water was placed in the beaker, the current increased to the value shown by the second maximum. A full beaker of liquid air gave the third maximum, but the current returned to its original value when the air was removed; when again dipped in air, the fourth prominent maximum was obtained. With water at room temperature the next maximum was found. A beaker of carbon tetrachloride raised about the cell gave the last maximum. The variation when the liquid air is removed is due probably to fog or mist in the air and on the glass immediately after the removal of liquid air. The constancy of total current at $12{\cdot}6 \times 10^{-6}$ ampere from this cell at room temperature over such a long period as that shown on the curve when the cell is subjected to such intense light as required to give this current is, I think, worthy of note.

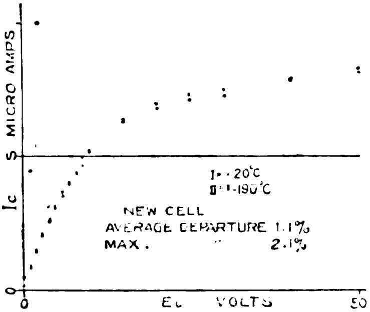
The foregoing experiments were thought to be good evidence that the increases were due to scattered light from the liquid and beaker. To test this more thoroughly, blackening the bulb with paint, lamp-black, and other things was tried. Cracked cells and cracked paint were the usual results, but finally a cell with the bottom wrapped in black paper gave the results shown in fig. 2.

Fig. 2.



The light used in this case was a 250 watt stereopticon lamp. Fig. 2 shows current plotted against time. The cell was at room temperature except for the time embraced by the double arrows. It will be seen from a glance at the points marked A that when the bulb was immersed in liquid air no appreciable change in the value of the photo-current resulted. This seems to show quite conclusively that if there is any temperature effect upon the photo-sensitiveness of sodium between liquid air and room temperature, it must be an extremely small one.

Fig. 3.



During the time-intervals indicated in fig. 2 by I and II two complete photo-current potential curves were taken. These curves are shown in fig. 3, the dots representing the curve taken at 20° C. and the arrowheads that at −190° C. It will be seen that the two curves are everywhere practically coincident, though there are four points which show a systematic difference all in the same direction. The actual readings in the case of both curves are shown in Table I.

Table I.

Voltage. Ec.	Photo-current. Room Temp. I_{20}.	Photo-current at −190° C. I_{-190}.
50	8·25	8·20
40	7·80	7·82
30	7·35	7·44
25	7·10	7·26
20	6·80	6·95
15	6·37	6·31
10	5·10	5·20
9	4·70	4·84
8	4·38	4·40
7	3·97	3·99
6	3·52	3·56
5	3·06	3·10
4	2·60	2·62
3	2·07	2·10
2	1·18	
1	·88	·80
0	·20	·28

These observations are taken in the same way as those recently published by H. E. Ives, but fail to show any such variations with temperature as he found.

Fig. 4 is a continuation of the photo-current time curve begun in fig. 2. At the time marked "Air off 2nd trap" the pump was disconnected from the system by a mercury cut-off close to the pump, and at the same time the liquid air was removed from that one of the two liquid-air traps in series which was nearest to the bulb and which had been cooled a considerable time after the first liquid-air trap had been functioning. The object of removing this liquid-air trap was to allow a very minute amount of impurity to flow back into the bulb. The effect of this impurity was observed instantly by an increase in current as shown by the arrow in fig. 4 above the comment "Air off 2nd trap." A voltage-current curve was taken at III, and then the cell was cooled in liquid air and a large increase in total current occurred; another voltage-current curve was taken at IV.

Fig. 4.

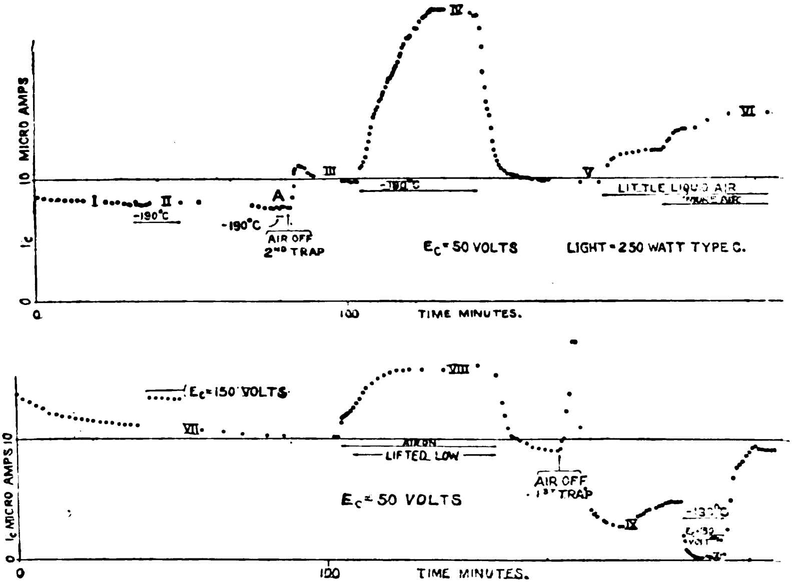
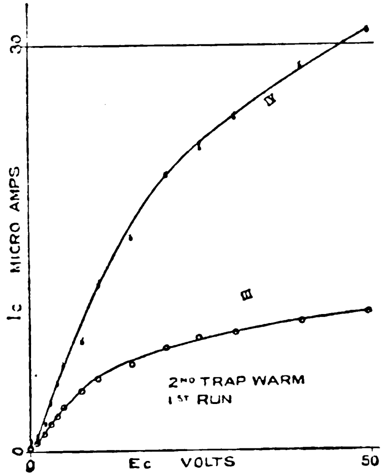
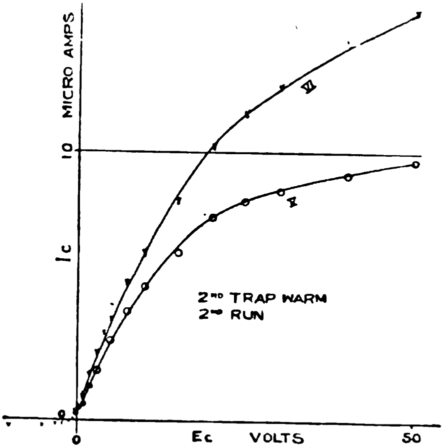


Fig. 5.



These last two are shown in fig. 5. Liquid air was then removed and other similar curves were taken at V and VI, and they are plotted in fig. 6. The same current-time curve, taken the following day, is continued at the bottom of fig. 4. Voltage-current curves were taken at VII and VIII, the first at room, the latter at liquid air temperature. These last two curves are not reproduced since they were practically identical with V and VI.

Fig. 6.



At the point marked "Air off 1st trap," the liquid air was removed from the trap nearest the pump. This was the first trap to be cooled during evacuation, and hence contained much more condensed vapour. With illumination and the collector voltage constant, the photo-current at first doubled, then dropped to about one-third its former value, as shown in fig. 4. When it was believed constant at IX, another voltage-current curve was taken. Next it was cooled in liquid air, and this time a decided drop in the total current occurred. At X a voltage-current curve was again taken (fig. 7). Removal of the liquid air caused an increase in total current. Further experimenting on this cell was prevented by a crack which developed at this point in the bulb.

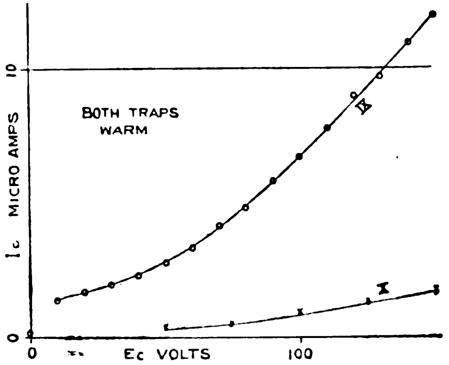
The question as to whether there may be minute traces of impurities in the sodium within the bulb of the sort not dependent upon residual gases or vapours has no bearing upon the main conclusion which is drawn below. For the sake, however, of obtaining evidence as to the possible existence of impurities coming through or out of the glass the following tests were made :—

1. An effort was made to drive both potassium and lithium through this glass without any success whatever.

2. A bulb of this kind was used as a sodium voltameter, and the correct atomic weight of sodium to one part in 500 was obtained. This limit of accuracy was set in this experiment simply by the uncertainty in the measurement of the quantity of electricity producing the deposit of sodium.

3. A sodium arc was formed in the bulb, and no trace of lines other than sodium obtained. The last test presumably means a purity of at least one part in 500,000.

Fig. 7.



Dr. Ives appears to find a temperature effect upon photo-currents from both sodium and potassium between these temperature limits. In the foregoing experiments it appears that when the utmost precautions are taken against contamination no temperature effect on photo emission from sodium is found. By contaminating the surface, however, both of the types of temperature effects which Dr. Ives obtains, namely, an increase in one case and a decrease in another, are found.

It is believed that the above evidence is convincing that:

(1) *The total photo-current of sodium is constant, within a few per cent. at most, over a temperature range* 20° *to* −190° *C., if the surface is sufficiently pure;*

(2) *if the surface is just slightly contaminated, it may be much more sensitive at low temperature than at room temperature*; *and*

(3) *if slightly more contaminated by some unknown vapour, the surface may be several times less sensitive at liquid air temperature than at room temperature.*

That the change of total photo-electric current within the temperature limits noted should be less than 1 per cent. for a pure surface is supported by some theoretical work of

Dr. J. R. Nielsen in this laboratory. This work has been submitted for publication in the Physical Review.

I wish to acknowledge with thanks the suggestions, advice, counsel, and inspiration of the Director of this Laboratory, Professor Robert A. Millikan.

Norman Bridge Laboratory of Physics,
California Institute of Technology,
Pasadena, California.
October 30, 1924.

CXVII. *The Broadening of Lines in Arc Spectra and the Stark Effect.*

By H. LOWERY, *M.Sc.* (*Lond.*), *A.Inst.P.*, *F.R.A.S.*, *Assistant Lecturer in Physics, Manchester University*[*].

[Plate XII.]

Introduction.

IN a very interesting paper[†] on "The Broadening of Spectral Lines caused by Increased Current Density and their Stark Effects," Kimura and Nakamura give results of experiments on the broadening of lines in the arc spectra of copper, silver, gold, magnesium, calcium, chromium, and nickel produced by heavy currents of the order 40 amperes and upwards. The nature of the broadening is compared with the displacement and separation of the lines into components by a strong electric field (Stark effect), the results of the work on the Stark effect by Stark and Kirschbaum[‡], Anderson[§], Takamine[||], Howell[¶], Takamine and Kokubu[**], and Yoshida[††] being used for this purpose.

The general conclusion arrived at from this comparison was that "the lines showing the Stark effect were generally broadened easily in the spectrum of a heavy current arc ...... The lines showing displacements towards the red side in the Stark effect broadened on the red side when the current density was greatly increased in the arc ...... Similarly, the lines showing displacement towards the violet side in the Stark effect broadened on the violet side. The lines having isolated components generally developed broadened lines at the position of such components."

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[*] Communicated by Prof. W. L. Bragg, F.R.S.

[†] Jap. Jour. of Phys. ii. No. 3-5, p. 61 (1923).

[‡] *Ann. d. Phys.* xliii. p. 1030 (1914).

[§] Astrophys. Jour. xlvi. p. 104 (1917).

[||] Astrophys. Jour. l. p. 27 (1919).

[¶] Astrophys. Jour. xliv. p. 87 (1916).

[**] Mem. Coll. Sci. Kyoto Imp. Univ. iii. p. 173 (1918).

[††] Mem. Coll. Sci. Kyoto Imp. Univ. iii. p. 287 (1918).

In a previous paper * the present writer has described experiments in which spectroscopic observations were made upon the interrupted silver, gold, and copper arcs, using the method adopted by Hemsalech and de Gramont † in their study of the occurrence of enhanced lines in the arc. The experiments were originally begun with the object of investigating the existence of the Stark effect in the arc and, in the paper referred to, attention was drawn to the widening of the lines in the arc spectrum of silver in the region near the fixed pole where presumably the electric fields are very intense during the early stages of the arc flash.

In view of the distinct broadening of lines in arc spectra produced under two apparently different sets of conditions, viz. : (1) those due to a heavy current (voltage 110 volts) as in the experiments of Kimura and Nakamura, and (2) those obtaining in the interrupted arc, it will be of interest to compare the nature of the broadening in the two cases and to consider the results in connexion with the Stark effect.

Experimental Results.

The *interrupted* arc spectra of silver, gold, copper, nickel, and iron were investigated. Kimura and Nakamura give results of their experiments for all these metals except iron. The nature of the broadening in the experiments with the interrupted copper, silver, and gold arcs is given in the following tables (I, II, and III). Symmetrical broadening is indicated by vr or VR. The symbols vR, Vr, v, r, V, R denote the different kinds of unsymmetrical broadening respectively, a single letter indicating broadening on one side only. The large and small letters are employed to show in a general way the relative sizes of the wings. The extent of any wing from the original line is usually of the order 1 to 5 A.U., but accurate determinations of the size of the wings are not possible owing to their diffuse edges. Intensities range from 0 (weakest) to 10 (strongest).

The last column in the tables indicates the nature of the broadening obtained by Kimura and Nakamura in their experiments.

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* Phil. Mag. xlviii. p. 1122 (Dec. 1924).

† Phil. Mag. xliii. (Feb. and May 1922).

TABLE I.—Copper.

Series formula.	Wave-lengths in I.A.	Nature of broadening (interrupted arc).	Intensity (interrupted arc).	Nature of broadening (Kimura and Nakamura).
$1\pi_2-4\delta'$	3654·3	vr	6	Wing on red side.
$1\pi_2-4\sigma$	3825·05	v	2	Feeble intensity. Broadening not recorded.
$1\pi_1-4\sigma$	3861·75	v	2	Feeble intensity. Broadening not recorded.
	3894·49	vr	1	Feeble intensity. Broadening not recorded.
$1\pi_2-3\phi$	4015·8	v	1	One sided (violet) wing.
$1\pi_2-3\delta'$	4022·67	vR	10	Red (bright) & violet (faint) wings.
$1\pi_1-3\varphi$	4056·7	V	4	One-sided (violet) wing.
$1\pi_1-3\delta$	4062·69	vR	10	Red (strong) & violet (faint) wings.
$1\pi_1-3\delta'$	4063·30	(v ?) r	2	Red (strong) & violet (faint) wings.
$1\pi_2-3\sigma$	4480·38	R	9	Not recorded.
$1\pi_1-3\sigma$	4530·84	R	10	,, ,,
$1\pi_2-2\delta'$	5153·23	V	10	,, ,,
$1\pi_1-2\delta$	5218·17	V	10	,, ,,

Note on Table I.—Copper.

It is assumed that the line λ 4062·69 (I.A.) of intensity 10 is identical with the line λ 4062·14 of Takamine and of Kimura and Nakamura.

Note on Table II.—Silver.

λλ 4210·71, 4212·60. In describing the broadening of these two lines in their experiments, Kimura and Nakamura say, "The images of these lines presented an appearance similar to the self-reversal of a single spectral line, the violet components of the former line and its red component together with the corresponding one of the latter forming wings on both sides."

In the interrupted arc the space between the two lines at the beginning of the flash is hazy, and might be regarded as

TABLE II.—Silver.

Series formula.	Wave-length in I.A.	Nature of broadening (interrupted arc).	Intensity (interrupted arc).	Nature of broadening (Kimura and Nakamura).
$1\pi_2--4\delta'$	3682·30	vr	5	Bright violet and faint red wings.
$1\pi_1—4\delta$	3810 71	vr	5	Bright violet and faint red wings.
$1\pi_1—3\sigma$	3981·72	r	6	One-sided (red) wing.
$1\pi_2—3\delta'$	4055·31	VR	10	Broad red wing and diffuse violet component.
$1\pi_1—3\delta$	4210·71	Vr	10	(See note below).
$1\pi_1—3\delta'$	4212·60	vR	10	" "
	4226·39	r	5	Faint shading on red side.
$1\pi_2—3\sigma$	4476·12	r	8	Slight broadening on red side.
$1\pi_1—3\sigma$	4668·52	r	8	Not recorded.

filled with a wing on the red side of λ 4210·71, or with a wing on the violet side of λ 4212·60, or even with two such wings either superimposed or meeting each other at their edges.

TABLE III.—Gold.

Wave-length in I.A.	Nature of broadening (interrupted arc).	Intensity (interrupted arc).	Nature of broadening (Kimura and Nakamura).
3796·00	Vr	8	Broadening toward violet side.
4084·14	r	8	Slight broadening toward the red.
4128·65	r	4	Faint, but slightly diffuse both sides.

In the above tables the broadening in the interrupted arc spectra is given only for those lines on which the Stark effect has been observed, though many other lines, in the case of each metal, exhibited traces of broadening at the beginning of an arc flash. The copper lines λλ 3687, 3689, 3830, and the silver lines λλ 3841, 4081, 4207 (on all of which the Stark effect has been observed), were so feeble in all the photographs that no definite statement can be made with regard to their possible broadening.

Comparison and Discussion of Results.

The above tables show that the broadening of lines in the interrupted arc spectra at the beginning of an arc flash is practically of the same nature as Kimura and Nakamura obtained in their experiments with the steady arc. The broadening of the following lines is not given by Kimura and Nakamura, the first three lines being very faint in their plates, the remainder falling outside the region of their investigation :—Copper: λλ 3825, 3862, 3895, 4480, 4530, 5153, 5218 ; Silver : λ 4668. The broadening of all these lines in the interrupted arc is given in the above tables and, with the slight exception of λ 3895 (copper), agrees with the expected broadening from considerations of the Stark effect.

In order to illustrate more fully the nature of the comparison between the broadening of the lines and their Stark effects, a portion of Takamine's table on the Stark effect for copper is given, together with the broadening effect under the interrupted arc conditions, where it will be seen that there is a general good agreement between the results. The positive and negative signs in the second and fourth columns refer to the components on the red and violet sides of the lines in question.

Table IV.—Copper.

λ (I.A.).	*p*-comp.		*n*-comp.		Broadening (interrupted arc).	Intensity.
	Δλ.	Intensity.	Δλ.	Intensity.		
3825·05	−0·16	3	−0·10	3	v	2
3861·75	−0·11	3	−0·12	3	v	2
3894·49	+0·27	1	+0·23	1	vr	1
4015·8	−0·47	2	−0·43	2	v	1
4022·67	+0·46	7	+0·33	7	vR	10
4056·7	−0·62	3	−0·6[illegible]	3	V	4
4062·69	+0·60	10	+0·44	10	vR	10
4063·30	+0·37	4	+0·33	4	(v ?) r	2
4480·38	+0·09	6	+0·11	6	R	9
4530·84	+0·04	6	+0·03	6	R	10
5153·23	−0·10	6	−0·05	6	V	10
5218·17	−0·09	10	−0·07	10	V	10

It may be noted further that, at least in the interrupted arc experiments, without exception the lines of the diffuse series are broadened to a greater extent than those of the principal and sharp series. In addition, as in Takamine's work, the lines of the diffuse series for silver are affected on both sides, thus differentiating these lines from those of the sharp series which are affected on one side only.

Nickel and Iron.

Kimura and Nakamura examined the nickel arc under a heavy current but did not find any well-marked broadening of lines as in the case of copper, silver, and gold, though such broadening would be expected as many nickel lines show the Stark effect *. In the *interrupted* arc spectra, any broadening which existed was of such a small order that no definite statement of its nature can be given. Iron was also one of the metals examined in the interrupted arc and the results were as in the case of nickel. It may be noted here that Takamine states that the Stark effect for iron is exceedingly small compared with that for other elements.

Magnesium.

Probably the most striking agreement between the results obtained by Kimura and Nakamura and those of the interrupted arc experiments is to be found in the metal magnesium. The interrupted arc spectrum of this metal was studied by Hemsalech and de Gramont † during their research on the occurrence of enhanced lines in the arc. They give a photograph (plate xviii. *loc. cit.*) of the interrupted magnesium arc spectrum over a region including the lines λλ 4352, 4571, 4703, which shows the first and third lines with well-marked wings developed on the red side as in the experiments of Kimura and Nakamura. Though the second line λ 4571 is displaced to the red in the Stark effect, it appears fairly sharp on the photographs of the heavy current arc. The photograph of Hemsalech and de Gramont referred to above shows this same line quite sharp in the interrupted arc!

In view of the close connexion which the above experimental results seem to indicate between the broadening of lines in the arc spectra and the Stark effect, it is interesting to review Duffield's ‡ experiments on the effects of pressure on arc spectra when the principal effect noted was a broadening of many of the lines. Duffield records that at high pressures the metal arcs he examined were frequently blown out by the luminous metallic vapour which they expelled, so that "a single exposure was the integrated effect of a number of short-lived arcs." The spectra obtained were therefore those of interrupted metal arcs under high pressures, and the broadening effect observed in the spectra was the net result of conditions similar to those referred to above in addition to those of the high pressures employed. Duffield recognized that effects might possibly be produced in the spectra of the metal arcs under high pressure owing to the necessity for frequently bringing the poles into contact to strike the arc, for he says: "In the experiments with the iron arc the chief variables were the current strength and the length of the arc, which, on account of the necessity for continually striking the arc, could not be kept constant. The variables dependent upon these are the temperature, potential gradient, the quantity, and perhaps the density of the material in the arc."

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* Takamine, Astrophys. Jour. l. p. 33 (1919).

† Phil. Mag. xliii. (May 1922).

‡ Phil Trans, A. ccix. p. 205 (1908); ccxi. p. 33 (1911).

The facts brought out by the experiments with the interrupted arc prove conclusively that the effects due to the striking of the arcs cannot be neglected in considering Duffield's results. Further, in the light of the results given by Kimura and Nakamura, since the current in the steady metal arcs of Duffield sometimes reached the value of 20 amperes, it is highly probable that the effect of such a high current density in these arcs cannot wholly be neglected in interpreting the broadening of lines in Duffield's photographs.

Finally, in connexion with the Stark effect interpretation of the broadening of lines in arc spectra, it may be pointed out that Nagaoka and Sugiura* have developed a method of observing the Stark effect by means of the arc which is more convenient than the original method involving the use of a vacuum tube. They used a special device to keep the arc steady in the vertical position. The lines originating in the lower electrode extending from the visible part of the spectrum down to the ultra-violet showed distinct separation which was identical with the Stark effect observed with vacuum tubes. It was found convenient to work with a 500 volts arc, though the effect can be observed at 100 volts.

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* 'Nature,' cxi. p. 431 (1923).

Explanation of Plate.

The photograph is reproduced from one of the negatives obtained when arc flashes were made between copper poles in oxygen at 350 volts and initial current 5 amperes, the lower fixed pole being negative.

Summary.

1. Attention is drawn to the similarity of the broadening of lines as produced (1) in the interrupted arc spectra of copper, silver, gold, nickel, and magnesium, (2) in the heavy current arc spectra of Kimura and Nakamura.

2. The broadening is such as would be expected from observations on the Stark effect.

3. It is pointed out that, in interpreting the broadening of lines obtained by Duffield in his experiments on the effect of pressure on arc spectra, it is necessary to take into account the effects due to the heavy currents he employed and the necessity for repeatedly striking the arc.

Again I desire to express my thanks to Dr. G. A. Hemsalech for his helpful advice while the experiments on the interrupted arc were in progress, and also to Professor W. L. Bragg, F.R.S., for his encouragement during the research.

Physics Dept.,
The University of Manchester,
Jan. 1925.

[*Note.*—A comprehensive account of the experiments and results of Nagaoka and Sugiura, mentioned above, is to be found in the Japanese Journal of Physics, vol. iii. Nos. 1–3, 1924.]

CXVIII. *On the Stabilization of Instable Equilibrium by means of Gyroscopic Forces.*—II. *By* Dr. H. J. E. Beth (*Deventer*) *.

IN a preceding paper † I have proved that for the case of an even number of irrotational instabilities the equilibrium of a system with an arbitrary number of degrees of freedom may be converted into a stable one by the means of gyroscopic forces. In the present paper I wish to show

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* Communicated by the Author.

† Phil. Mag. February 1925.

how the subject may be investigated more in detail for the cases of a mechanism with three or four degrees of freedom with the help of geometrical considerations.

Three degrees of freedom.

If in the determinantal equation

$$\Delta \equiv \begin{vmatrix} m^2+a_{11} & g_{12}m & g_{13}m \\ -g_{12}m & m^2+a_{22} & g_{23}m \\ -g_{13}m & -g_{23}m & m^2+a_{33} \end{vmatrix} = 0,$$

we write

$$P = \sqrt[3]{a_{11}a_{22}a_{33}}, \quad u = \frac{m^2}{\sqrt{a_{11}a_{22}a_{33}}};$$

$$X = \frac{\Sigma a_{11} + \Sigma g_{23}^2}{P}, \quad Y = \frac{\Sigma a_{22}a_{33} + \Sigma a_{11}g_{23}^2}{P^2};$$

it passes into

$$u^3 + Xu^2 + Yu + 1 = 0. \quad . \quad . \quad . \quad . \quad (1)$$

As we have supposed that the system has an even number of irrotational instabilities, we may suppose a_{11} and a_{22} to be negative, a_{33} positive. We ask how the gyroscopic force must be chosen in order to make the roots of (1) negative.

We first investigate the influence of the coefficients g_{23}, g_{31}, and g_{12} on the nature and the sign of the roots of (1). With this aim, we associate the equations (1) with the points of a plane determined by their rectangular coordinates. As the roots of (1) never become zero or infinite, a change of sign of the roots occurs only when we pass twice the locus δ of the points (X, Y), for which (1) has equal roots.

This locus δ, represented by the equation

$$\delta \equiv X^2Y^2 - 4X^3 - 4Y^3 + 18XY - 27 = 0, \quad . \quad . \quad (2)$$

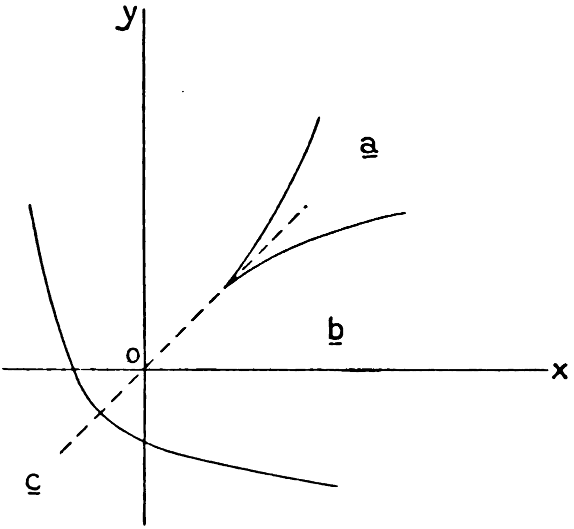
has been drawn in fig. 1. It divides the plane in three regions, viz. the region a of three negative roots, the region b of one negative and two imaginary roots, and the region c with one negative and two positive roots.

The equation (1) represents a system of straight lines containing a parameter u; $-u$ is the parameter of direction of such a line; δ is the envelope of the system. Through any point of the plane three tangents at δ pass. For a point in a the three tangents have a positive slope; for a point in b there is only one real tangent which has a positive slope; for a point in c there are two tangents with negative and one with positive slopes.

a is the region of the stable positions of equilibrium. The irrotational equilibrium being instable, its image-point in the XY-plane is a point $Q_{irr.}(X_0, Y_0)$ in *c*, and

$$X_0 = \frac{\Sigma a_{11}}{P}, \quad Y_0 = \frac{\Sigma a_{11} a_{22}}{P^2}.$$

Fig. 1.



By the means of gyroscopic forces, the position of equilibrium passes into

$$X = X_0 + \frac{\Sigma g_{23}^2}{P}, \quad Y = Y_0 + \frac{\Sigma a_{11} \cdot g_{23}^2}{P^2}. \quad . \quad . \quad . \quad (3)$$

The image-point moves in the direction :

$$\lambda = \frac{Y - Y_0}{X - X_0} = \frac{1}{P} \frac{\Sigma a_{11} g_{23}^2}{\Sigma g_{23}^2} = \frac{\Sigma - u_{1_0} g_{23}^2}{\Sigma g_{23}^2}, \quad . \quad . \quad (4)$$

where u_{1_0}, u_{2_0}, and u_{3_0} are the roots u corresponding with the point $Q_{irr.}$.

From this it follows that the directions in which the image-point may move by reason of the gyroscopic force are limited by those two magnitudes of $-u_{1_0}$, $-u_{2_0}$, and $-u_{3_0}$, which include the third, and that any direction within the angle determined by the two corresponding tangents at δ is a possible one.

We therefore draw from $Q_{irr.}$ at δ the two tangents having the greatest and the smallest coefficient of direction. Of the tangents we take the half-lines with positive X-components (according to (3) $X-X_0$ is always positive). The angle within these two half-lines contains all image-points which may be reached by the means of gyroscopic forces. The result may be stated in still simpler terms: we draw from $Q_{irr.}$ the tangent at the border of region a; *the part of a below this tangent contains the points we may reach.*

From this we conclude again that it is always possible to stabilitate the two irrotational instabilities; moreover, we observe that from fig. 1 it follows at once that by means of gyroscopic forces stability may never be disturbed (when the irrotational equilibrium is stable, its image-point is in a and the angle between the limiting tangents is also entirely within a).

Returning to the case of instable irrotational equilibrium, we have still two different cases to consider, viz. 1° $Q_{irr.}$ is below the line $Y=X$, 2° $Q_{irr.}$ is above the line $Y=X$. In the second case the part of region a we may reach consists of two different parts, α' and α'', of different character. When in this case a direction of motion for the image-point is given in order to enter into a it will for the first time enter into a in a point of α', but it will leave the region a again and enter into it for the second time in a point of α''. We will neglect the part α' and occupy ourselves only with α''. We therefore speak only of stabilization by the means of gyroscopic forces when the equilibrium remains stable as long as the angular velocity of the flywheels is beyond a minimum value (figs. 2 a and 2 b).

If ξ, η, and ζ are the principal coordinates of the mechanical system, we may introduce a representative point of which the rectangular coordinates are ξ, η, and ζ. The components of the gyroscopic force along the axes are given by

$$K_\xi = -g_{12}\dot{\eta} + g_{13}\dot{\zeta},$$

$$K_\eta = -g_{23}\dot{\zeta} + g_{12}\dot{\xi},$$

$$K_\zeta = -g_{13}\dot{\xi} + g_{23}\dot{\eta}.$$

The gyroscopic force is the vector-product of the velocity of the representative point and the vector G, of which the ξ-, η-, and ζ-components are g_{23}, g_{31}, and g_{12}.

Fig. 2 *a*.

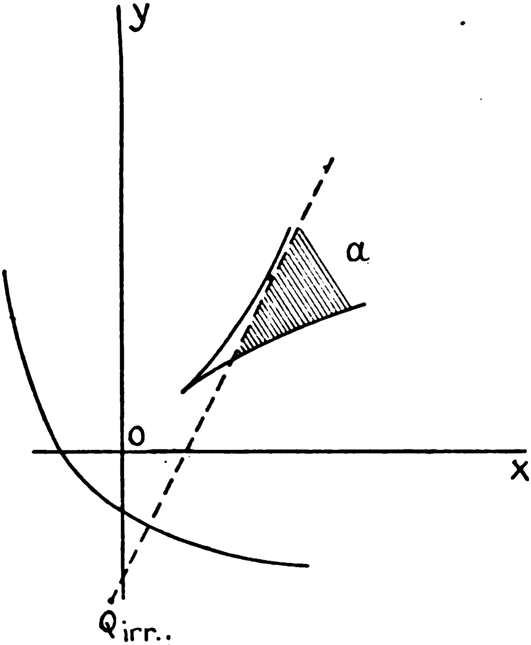
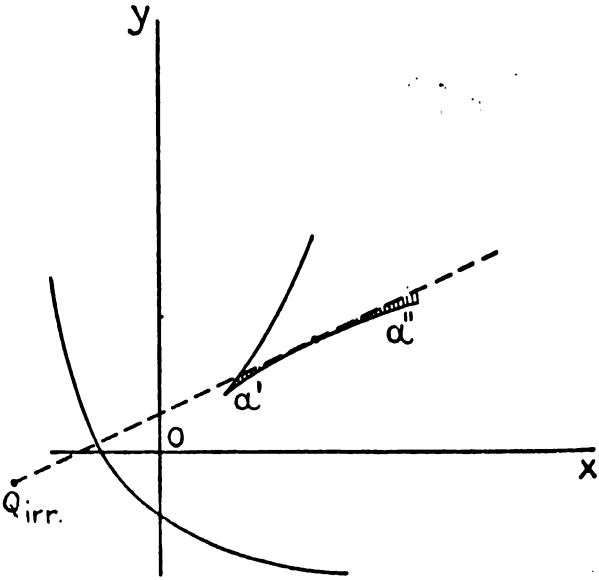


Fig. 2 *b*.



We first consider this vector $G(g_{23}, g_{31}, g_{12})$. Its direction in space is not determined by the direction of motion

$$\lambda = \frac{Y-Y_0}{X-X_0}$$

in the plane of δ. From (4) we deduce that the direction of G belonging to a given λ is an arbitrary generatrix of the quadratic cone

$$\lambda(\xi^2+\eta^2+\zeta^2)+(u_{1_0}\xi^2+u_{2_0}\eta^2+u_{3_0}\zeta^2) = 0,$$

or

$$(\lambda+u_{1_0})\xi^2+(\lambda+u_{2_0})\eta^2+(\lambda+u_{3_0})\zeta^2 = 0.$$

We suppose u_{3_0} to be the negative root for $Q_{\mathrm{irr.}}$. Then the directions λ that may bring the image-point in the XY-plane into the region of stability a are between the limits $-u_{3_0}$ and zero (when $P_{\mathrm{irr.}}$ is above the line $Y=X$, we consider only the part a'').

For $\lambda=-u_3$ the cone has contracted into the ζ-axis (axis of stability). All cones of the pencil for $0<\lambda\leq-u_{3_0}$ have their real axis along the ζ-axis, do not intersect each other, and fill up the space within the cone V :

$$u_{1_0}\xi^2+u_{2_0}\eta^2+u_{3_0}\zeta^2 = 0,$$

or

$$V \equiv a_{11}\xi^2+a_{22}\eta^2+a_{33}\zeta^2 = 0,$$

where V represents the potential function of the positional forces. *Any line passing through* O *and at the inside of* V *represents a possible position of the vector* $G(g_{23}, g_{31}, g_{12})$; the generatrices G of a similar cone of the pencil correspond to a similar direction λ in the plane of δ.

The magnitude of G is given by (3),

$$\sqrt{(\Sigma g_{23}^2)} = \sqrt{\frac{1}{P}}(X-X_0).$$

As P is a constant (for the same irrotational equilibrium), the magnitude of the vector G is proportional to the square root of the X-component of the displacement in the plane of δ. With the help of fig. 2 (or by the solution of a biquadratic equation) we are able to find the minimal value of G with any possible direction λ; the minimum minimorum we have for $\lambda=-u_{3_0}$, for which value of λ G has the ζ-direction.

We now proceed to the gyroscopic force F itself. As G is a fixed line during the motion, the force F remains parallel with a fixed plane U normal to G. From the possible directions of G we deduce that *all planes* U *are possible which have with the supplementary cone* C′ *of cone* V :

$$C' \equiv \frac{\xi^2}{a_{11}} + \frac{\eta^2}{a_{22}} + \frac{\zeta^2}{a_{33}} = 0$$

an elliptical intersection. With any possible plane U is associated a value of λ. When the motion of the representative point is projected on a plane U, the gyroscopic force in any point is normal to the velocity of the projection and equal to the product of this velocity and a constant factor G which has for any plane U a minimum value. This constant has the smallest value if U is the plane of the instabilities.

Four degrees of freedom.

For this case the determinantal equation $\triangle = 0$ has the form

$$u^4 + Xu^3 + Yu^2 + Zu + 1 = 0, \quad . \quad . \quad . \qquad (5)$$

where

$$P = \sqrt[4]{a_{11}a_{22}a_{33}a_{44}}, \qquad u = \frac{m^2}{P}.$$

$$X = \frac{\Sigma a_{11}}{P} + \frac{\Sigma g_{12}{}^2}{P^2},$$

$$Y = \frac{\Sigma a_{11}a_{22}}{P^2} + \frac{\Sigma(a_{11}+a_{22})g_{34}{}^2}{P^3} + \frac{(\Sigma g_{12}g_{34})^2}{P^4},$$

$$Z = \frac{\Sigma a_{11}a_{22}a_{33}}{P^3} + \frac{\Sigma a_{11}a_{22} \cdot g_{12}{}^2}{P^4}.$$

($\Sigma g_{12} \cdot g_{34}$ is written instead of $g_{12}g_{34} - g_{13}g_{24} + g_{14}g_{23}$.)

We have to consider two cases: 1° two of the coefficients a_{11}, a_{22}, a_{33}, and a_{44} are negative, and 2° the four coefficients are negative.

We may associate the equations (5) corresponding to different values of X, Y, and Z with the points of space. As no root of (5) may become zero or infinite, a change of the sign of the roots occurs only by passing twice the locus of the points, where (5) has equal roots. This locus or discriminantal surface is the developable ruled surface which is enveloped by the variable plane (5).

A discriminantal surface for the biquadratic equation has been introduced by Kronecker[*]; however, his equation has not the form of (5): the number of parameters has been reduced by him by expelling the term with u^3; the surface arising in this way is not applicable for the present investigation. A description of the discriminantal surface for the equation (5) is to be found elsewhere [*], and the regions are indicated in which the surface divides space. There are six regions corresponding with the nature and the sign of the roots of (5): 4 imaginary roots, 2 positive 2 negative roots, 2 imaginary 2 positive roots, 2 imaginary 2 negative roots, 4 positive roots, 4 negative roots.

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[*] *Monatsberichte der Berliner Akademie,* 14 February, 1878.

The image-point $Q_{\text{irr.}}$ for the irrotational equilibrium is lying either in the region of 4 positive roots or in the region of 2 positive and 2 negative roots. We have to inquire whether in both cases it is possible to displace the image-point into the region of stability, viz. the region of 4 negative roots.

For this aim we have to investigate the displacements:

$$X-X_0=\frac{\Sigma g_{12}^2}{p^2},$$

$$Y-Y_0=\frac{\Sigma(a_{11}+a_{22})g_{34}^2}{p^3}+\frac{(\Sigma g_{12}g_{34})^2}{p^4},$$

$$Z-Z_0=\frac{\Sigma a_{11}a_{22}g_{12}^2}{p^4},$$

which may be executed with the help of the gyroscopic forces. We see at once that the question is much more intricate than for the case of three degrees of freedom, because the expressions for the displacement of the image-point are no longer homogeneous with respect to the coefficients g. For small values of the g we first can neglect the term which disturbs the homogeneity, and we may find that the points we are able to reach lie inside a three-sided pyramid. For large values of the g, the neglected term becomes predominant when the inequality is fulfilled,

$$\Sigma g_{12}g_{34}\neq 0. \qquad (6)$$

These considerations, in connexion with an inspection of the discriminantal surface, will show that stabilization may always be obtained by sufficient values of the g, provided (6) be obeyed, for two and four instabilities.

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[*] Christiaan Huygens, 1925.

CXIX. *The Mass-Spectra of Chemical Elements.*—Part VI. *Accelerated Anode Rays Continued.* *By* F. W. Aston, *Sc.D., F.R.S., Fellow of Trinity College, Cambridge*[*].

IN Part V. of this series of communications[†] the method of accelerated anode rays was described by which the mass-rays of a large number of metallic elements were produced in a form suitable for analysis by the mass-spectrograph. The present paper contains the results of further investigations by the same method during the year 1924. Although the anode ray discharge tube had to be repeatedly rebuilt during this period for purposes of cleaning and replacement its general design has not been altered substantially from that already illustrated[‡]. The only change in detail worthy of note consists of setting back the surface of the composite anode several millimetres from the mouth of the pyrex tube containing it. This appears to result in a thinner but more concentrated beam of rays, but can only be advantageously applied in the fortunate circumstance of the beam being truly axially directed down the slit system of the spectrograph. As before, the extension of the method to new, and generally heavier, elements becomes increasingly difficult and the advances recorded here are nearly all dependent on the use of highly sensitive plates made by a schumannizing process recently described[§]. The successes obtained by incorporating the elements themselves into the anode, in the cases of tellurium and bismuth were to some extent unexpected and are probably due to the particular range of boiling points exhibited by these elements.

During the experiments on lead which only gave inconclusive results it was realized that the useful limit of work with the mass-spectrograph in use had been reached and it has now been dismantled to make room for a new one. The latter has been designed to give higher resolution and, more particularly, greater accuracy of measurement. If successful it will be used rather for the more exact comparison of the masses of known lines, with a view to determining their divergencies from the whole number rule, than for the analysis of more elements. This paper is therefore the last of the series and for that reason a complete list of all non-radioactive isotopes so far discovered is included in it.

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[*] Communicated by the Author.

[†] Phil. Mag. xlvii. p. 385.

[‡] *Loc. cit.* p. 387.

[§] F. W. Aston, Proc. Camb. Phil. Soc. xxii. p. 548 (1925).

Indium (At. Wt. 114·8).

Indium is chemically very similar to gallium. It was therefore expected to yield to the same treatment. The fluoride was prepared from a sample of the metal kindly supplied by Professor T. W. Richards of Harvard, by solution in hydrofluoric acid. This incorporated into the anode gave a mass-spectrum showing one line only at 115. The mass of this appeared integral when compared with the lines of iodine and cæsium. No great accuracy is claimed for these measurements and the line is too faint to exclude the possible presence of another isotope. Until further evidence is available on this point, indium is best regarded as a simple element of mass number 115.

Further experiments with Strontium.

The very bright anode beam given by this element* puts it next to lithium in value as a component of anode mixtures used in testing the setting of the discharge tube. In consequence many mass-spectra of it have been obtained. The more recent of these, though they confirm the previous conclusion that this element consists almost entirely of atoms of mass number 88, explain to a large extent the low value of its chemical atomic weight. In the first place the best plates give evidence of an extremely faint isotope 86 which appears to be present to the extent of about 3 or 4 per cent. In the second place the most accurate determinations of the mass of its principal constituent suggest that it is decidedly less than a whole number. For this purpose the lines of iodine and bromine were employed for reference. The chemical atomic weights of these elements (79·916 and 126·932) are used as substandards and have been determined with exceptional accuracy. The results of the mass-spectrograph indicate that we may confidently regard iodine as a simple element so that its line is taken as representing a mass of 126·93. The doublet of bromine has been recorded in all degrees of intensity on a large number of plates and, although the eye is particularly critical in judging the relative intensities of two similar images close together, no difference in intensity between the two components has been observed. It follows that its heavier isotope can be taken as of mass 80·92 with an accuracy at least exceeding one part in one thousand. Accepting these two values the strontium line gives the same mean figure 87·8 for each comparison. The presence of Sr^{86} will bring this down a further fraction so that the discrepancy between the mean atomic weight calculated from the mass spectra and that accepted from chemical work 87·65 is no longer very serious.

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* *Loc. cit.* p. 395.

Barium (At. Wt. 137·37).

The first successful experiments with barium were performed with anodes containing iodides and although they showed clearly that the mass number of its principal isotope was 138 the penumbra of the enormously strong and over-exposed iodine line prevented a critical search for lighter isotopes which its chemical atomic weight suggests. Work with other elements was therefore continued with lithium bromide replacing the iodide previously used for testing. By cleaning operations and continuous running with anodes free from iodine, this element was gradually eliminated from the apparatus until its line became sufficiently weak to warrant a further investigation of barium. In these experiments the anode consisted of a mixture of barium chloride and lithium bromide. Schumannized plates were used and the line Ba^{138} was obtained of very great intensity. Examination of the mass spectra showed that no mass number less than 136 could possibly be present to an appreciable extent. Slight asymmetry of the strong line suggested the possible presence, in very minute proportion, of 136, and since resolution in the neighbourhood of so strong a line is impossible on the instrument used, 137 may also be present. But even if both are present they cannot be so to an extent adequate to explain the chemical atomic weight now in use which appears therefore to be too low. In mitigation of this discrepancy, but not sufficient to explain it entirely, the principal line of barium, like that of strontium, appears to show a slight defect from a whole number mass.

Lanthanum (At. Wt. 138·91).

This rare earth element was investigated by means of its bromide which was prepared from a very pure specimen of the oxalate. A mixture of this with lithium bromide worked smoothly as an anode, but the results were not very intense. With an exposure of half an hour, however, a single line at 139 was obtained of such a strength as to make it reasonably certain that lanthanum is a simple element of mass number 139, as its chemical atomic weight would lead us to expect.

The plate was not suited to measurements of high accuracy but comparison with the iodine line showed no deviation from the whole number rule greater than that suggested by its atomic weight.

Praseodymium (At. Wt. 140·92).

The first experiments with this element using its fluoride were unsuccessful. Later, under better experimental conditions, results were obtained from the bromide made from a commercial sample (Schuchardt) of the oxide. The appearance of a line at 139 in addition to the one expected at 141 indicated that this was contaminated with lanthanum. Owing to the kindness of Dr. Auer von Welsbach, to whom the author is deeply indebted for a valuable collection of samples of rare earth salts, a specimen of the sulphate of praseodymium of exceptional purity was available. This was transformed into the bromide by treatment with strontium bromide and gave a single line at 141. It is therefore reasonably certain that praseodymium is a simple element of mass number 141. The chemical atomic weight, like that of lanthanum, suggests a mass slightly less than a whole number.

Neodymium (At. Wt. 144·27).

Neodymium bromide was prepared from a commercial sample (Drossbach) of the oxalate which, as results showed, was free from any serious contamination by neighbouring rare earth elements. The first attempts only yielded an indistinct band suggesting that the element was complex. Later, under particularly good experimental conditions with highly sensitive schumannized plates more definite effects were obtained. These indicated that neodymium certainly contains mass numbers 142, 144, and 146 not differing much in relative proportion, and possibly in addition (145) in smaller quantity. The latter must be regarded as doubtful for the present.

Cerium (At. Wt. 140·25).

Results from cerium were obtained by the use of the bromide prepared from a highly purified sample of the oxalate. Its most important mass line is 140 and shows no measurable deviation from a whole number. On the best mass spectra obtained a second fainter component 142 could be seen. The intensity of this line was in fair accord with the chemical atomic weight given above. Cerium may therefore be taken as a complex element with mass numbers 140 and 142. The latter is isobaric with the lighter component of its neighbouring element neodymium.

Zirconium (At. Wt. 91?).

A very large number of abortive attempts have been made to obtain the mass spectrum of this element. Some of these have been mentioned in previous papers in this series. One of the points of special interest in connexion with zirconium is the uncertainty of its atomic weight owing to the discovery of hafnium. The integer 91 has been adopted by the International Committee pending accurate determinations by chemical methods, work on which is still in progress. Success with the mass spectrograph was only obtained by the fortunate combination of an exceptionally favourable setting of the anode ray generator and a remarkably sensitive plate. The anode contained a mixture of zirconium fluoride and lithium fluoride, but a considerable quantity of bromine was left in the apparatus from previous experiments. Three of the lines appearing, 90, 92, 94, can be ascribed with confidence to zirconium. A fourth faint one at (96) is doubtful, but may be another isotope. As regards the relative intensities of the lines there is little to rely on, a very rough estimate is 10, 2, 4, (1), respectively. The masses corresponding to the first three can be determined with unusually high accuracy owing to the incidental appearance among them of a faint doublet 91, 93 due to CBr. There is no indication of any asymmetry in the spacing of the five lines 90–94 so that the masses of the isotopes of zirconium must be very closely integral with those of bromine. This by the argument already used on p. 1192 makes them less than whole numbers by about one tenth of a unit. Putting in these values and the relative intensities estimated above, we get for the mean atomic weight 91·2 or 91·4 according as we exclude or admit the presence of the doubtful (96), but little reliance is to be put on these figures.

Cadmium (At. Wt. 112·41).

This element, unsuccessfully attacked before, has now yielded to improved experimental conditions. Using an anode containing a mixture of cadmium fluoride and lithium fluoride prolonged exposure yielded a mass-spectrum showing satisfactory intensity and detail. This was fortunate, for cadmium is so complex an element and its lines so near the limit of resolution that without the enhanced resolving power given by the peculiar properties of the schumannized plates* it is doubtful if any reliable interpretation could have been made. Cadmium has six isotopes 110 (*c*), 111 (*e*), 112 (*b*), 113 (*d*), 114 (*a*), 116 (*f*). The relative intensities of the lines are indicated by the letters in alphabetical order, and agree reasonably well with the chemical atomic weight. The plates were not favourable for accurate determination of masses but these appear to be integral with that of iodine. It will be seen that the heaviest isotope is isobaric with the lightest isotope of tin the next higher element of even atomic number, but the most remarkable phenomenon observed is the extraordinary similarity between the groups of lines given by these two elements. If we except the still doubtful (Sn^{121}) and the heaviest isotope Sn^{124}, which does not appear to have its counterpart in the cadmium group, the intensity relations between the isotopes appear almost identical. The difference in mass number is 6, and if we place the lightest isotope at zero on the scale of mass number, each group will be found to consist of three strong even numbers 4, 2, 0 in descending order of intensity: then two nearly equal odd numbers 3, 1, and finally a fainter even number 6. This sequence of intensity relations is imitated, but less exactly, by selenium and krypton, and, quite possibly, by mercury. Such exact similarity as that exhibited by cadmium and tin is very significant and suggests that once the inner core of the nucleus, supposed the same for isotopes of the same element †, is formed the stability of nuclei produced by further additions to this core will be controlled by considerations which may be the same for cadmium as for tin.

Tellurium (At. Wt. 127·5).

Previous attempts to analyse this element by the use of its ethyl compound ‡, and by volatilizing the chloride and the element itself § had failed. Also during all the earlier work on accelerated anode rays any chance of success was improbable owing to the overwhelming strength of the iodine line the masking effect of which has already been referred to under barium. By the time the experiments on cadmium were complete iodine had been rigorously excluded from the apparatus for a long time, and although its line could still be seen and used for reference its intensity was sufficiently reduced to warrant a further attack on tellurium. A fragment of pure redistilled tellurium was pulverized and incorporated into the anode paste used in the experiments on cadmium. The lines of tellurium were at once obtained and the result was repeated and confirmed with an anode of tellurium, lithium fluoride, and graphite only. The effects were not strong but sufficient for identification and measurement. Tellurium gives three lines of even mass number 126, 128, 130. The intensities of the two latter appear about equal and double that of the first. The iodine line was too faint to be distinguished on these plates but comparative measurements could be made against the lines of bromine. These indicate that the masses may be a little less than whole numbers but there is no reason to suppose that the defect is abnormally great. Hence from the intensities of the lines it seems probable that the mean atomic weight is at least as high as 128. Owing to its anomalous position with regard to that of iodine (of which these results supply the obvious explanation) the atomic weight of tellurium has received an exceptional amount of attention from chemists and all their later determinations give a value considerably less than this. The discrepancy is of about the same order as that noted in the case of barium, but of the opposite sign. No explanation can be suggested in either case at present.

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* *Loc. cit.* p. 553.

† F. W. Aston, 'Nature,' 113, p. 395 (1924).

‡ Phil. Mag. xlii. p. 140 (1921).

§ Phil. Mag. xlv. p. 942 (1923).

Tellurium is unique among the elements so far analysed as it seems probable that *all* its mass numbers form members of isobaric pairs. They are shared by xenon, the element of next higher even atomic number.

Bismuth (At. Wt. 209·00).

The boiling point of bismuth is not much higher than that of tellurium so that there was some reasonable hope that it would yield to corresponding treatment. Metallic bismuth was ground into the anode paste and after a long exposure with the anode worked at a white heat it gave a single line in the position expected from its atomic weight. This line was very faint, and owing to the great mass lay in a part of the plate unfavourable for measurement, but comparisons with the lines of mercury leave little reason to doubt that bismuth is a simple element of mass number 209. Its atom is therefore the heaviest weighed on the mass spectrograph.

Further experiments on Silicon, Iron, and Lead.

Silicon.—In the first analysis of silicon * some evidence was adduced for the existence of an isotope Si^{30} but owing to the possibility of hydrides this could not be regarded as conclusive at the time. Later valuable support was obtained in the study of the band spectra of silicon compounds by Mulliken †. During one of the experiments on zirconium fluoride described in this paper the mass lines of silicon were obtained under conditions which precluded the presence of hydrides. In addition to the very strong line Si^{28} its two fainter companions Si^{29} and Si^{30} were clearly shown, the latter being rather less intense than the former in excellent agreement with the conclusions of Mulliken. Silicon may therefore be accepted as consisting of three isotopes. It is difficult to estimate the relative proportions accurately but the evidence of the mass-spectrograph is generally in favour of a mean atomic weight slightly higher than the one 28·06, recently adopted by the International Committee. The earlier value was 28·3.

Iron.—During some tests of a setting of the anode ray tube for efficiency, an anode containing bromide of iron was employed in the hope of obtaining the principal line Fe^{56} so strong that the question of the presence of the doubtful faint component Fe^{54} could be settled. Under such conditions the presence of a line at 54 could not be ascribed to adventitious organic or other molecules. On one occasion an exceptionally strong beam of rays was obtained and both lines appeared in an entirely satisfactory manner. The ratio of the line 54 to the predominant 56 could be roughly estimated at about 1 to 20. The most probable value of the mass of the latter has been given ‡ as 55·94. The presence of 5 per cent. of an isotope two units lighter will shift the atomic weight back by one tenth of a unit so that the results of the mass-spectrograph are in good agreement with the accepted atomic weight of 55·84.

Lead.—This element, which is of peculiar interest owing to our knowledge of its isotopes formed in radioactive disintegrations, has a boiling point not very much higher than that of bismuth and so might be expected to yield, though less easily, to the same treatment. Finely divided metallic lead scraped from a reduced negative accumulator plate incorporated into the anode mixture has given faint but positive

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* Phil. Mag. xl. p. 630 (1920).

† R. S. Mulliken, 'Nature,' 113, pp. 423, 489 (1924).

‡ Phil. Mag. xlv. p. 941 (1923).

Table of Elements and Isotopes *.

Element.	Atomic number.	Atomic weight.	Minimum number of isotopes.	Mass-numbers of isotopes in order of intensity.
H	1	1·008	1	1
He	2	4·00	1	4
Li	3	6·94	2	7, 6
Be	4	9·02	1	9
B	5	10·82	2	11, 10
C	6	12·00	1	12
N	7	14·01	1	14
O	8	16·00	1	16
F	9	19·00	1	19
Ne	10	20·20	2	20, 22
Na	11	23·00	1	23
Mg	12	24·32	3	24, 25, 26
Al	13	26·96	1	27
Si	14	28·06	3	28, 29, 30
P	15	31·02	1	31
S	16	32·06	1	32
Cl	17	35·46	2	35, 37
A	18	39·88	2	40, 36
K	19	39·10	2	39, 41
Ca	20	40·07	2	40, 44
Sc	21	45·1	1	45
Ti	22	48·1	1	48
V	23	51·0	1	51
Cr	24	52·0	1	52
Mn	25	54·93	1	55
Fe	26	55·84	2	56, 54
Co	27	58·97	1	59
Ni	28	58·68	2	58, 60
Cu	29	63·57	2	63, 65
Zn	30	65·38	4	64, 66, 68, 70
Ga	31	69·72	2	69, 71
Ge	32	72·38	3	74, 72, 70
As	33	74·96	1	75
Se	34	79·2	6	80, 78, 76, 82, 77, 74
Br	35	79·92	2	79, 81
Kr	36	82·92	6	84, 86, 82, 83, 80, 78
Rb	37	85·44	2	85, 87
Sr	38	87·63	2	88, 86
Y	39	88·9	1	89
Zr	40	(91)	3 (4)	90, 94, 92, (96)
Ag	47	107·88	2	107, 109
Cd	48	112·41	6	114, 112, 110, 113, 111, 116
In	49	114·8	1	115
Sn	50	118·70	7 (8)	120, 118, 166, 124, 119, 117, 122, (121)
Sb	51	121·77	2	121, 123
Te	52	127·5	3	128, 130, 126
I	53	126·92	1	127
X	54	130·2	7 (9)	129, 132, 131, 134, 136, 128, 130, (126), (124)
Cs	55	132·81	1	133
Ba	56	137·37	(1)	138
La	57	138·91	1	139
Ce	58	140·25	2	140, 142
Pr	59	140·92	1	141
Nd	60	144·27	3 (4)	142, 144, 146, (145)
Hg	80	200·6	(6)	(197), 202, 204, 198, 199, 200
Bi	83	209·00	1	209

* Including Dempster's results.

results. These indicate that common lead is a complex element, as was to be expected, but since there is little hope of obtaining definite information on its constitution with the apparatus used it has been decided to defer further investigation until a mass-spectrograph of higher resolving power is available.

Survey of Elements yet to be analysed.

It will be seen from the table that of the 80 non-radioactive elements known to exist, 56 have yielded fairly definite analyses. The experience gained during the work enables the probabilities of further progress to be estimated as follows:—

Niobium, molybdenum, rhodium, ruthenium, and palladium present great difficulties. All seem very unsuitable to the method of anode rays on account of their chemical properties. The first two might be attacked by the ordinary method by means of their volatile fluorides. Exactly the same reasoning applies to the corresponding elements tantalum, tungsten, osmium, iridium, and platinum but still greater difficulty is to be expected owing to their higher atomic weights. Elements 62–71 of the rare earths are all quite hopeful, faint effects have already been obtained from erbium (68), but a mass-spectrograph more suitable to rays of high mass number is desirable for their satisfactory analysis, just as for lead. Hafnium should be amenable to the form of treatment which succeeded with zirconium but some method of increasing the strength of the rays will have to be devised to overcome the adverse effect of greater mass, to which past failures are ascribed. A serious obstacle to the analysis of gold and thallium, which belong to groups reasonably favourable to anode ray production, is the purely technical one of eliminating mercury completely. Further difficulties in the case of gold are its inability to form compounds stable at high temperatures and its very high boiling point.

With regard to those elements only known in radioactive forms the majority cannot be directly investigated owing to the impossibility of obtaining sufficient material. Of the emanations, which being inert gases are particularly favourable to treatment in the discharge tube, radon only could be obtained in suitable quantity. The indirect evidence obtained from the study of radioactivity leaves very little doubt that it is simple of mass number 222 so that considering the disastrous after effects of the substance on the apparatus it is questionable if the experiment is worth while. Much the same arguments apply to radium itself which could be attacked on the same lines as barium, though probably with greater difficulty.

The parent elements thorium and uranium appear most hopeless of all for each is the heaviest member of a chemical group already found highly unfavourable to mass spectrum analysis. This is unfortunate for chemical evidence suggests that both are complex and a direct identification of their more important isotopes might be of the greatest value in explaining difficulties connected with the radioactive disintegration series.

In concluding this series of papers the author wishes again to express his cordial thanks to all who so kindly supplied materials for the analyses and to the Government Grant Committee of the Royal Society for some of the apparatus employed.

Summary.

Further investigations by the method of accelerated anode rays are described by which the constitutions of ten more elements Indium, Barium, Lanthanum, Praseodymium, Neodymium, Cerium, Zirconium, Cadmium, Tellurium, and Bismuth have been determined.

Evidence is given for an additional isotope of Strontium and isotopes of Silicon and Iron previously doubtful have been satisfactorily confirmed.

Some results have been obtained from lead but are not considered conclusive.

A general survey of the remaining elements is made and the possibility of their analysis discussed.

A complete list of all isotopes so far determined is given.

Cavendish Laboratory, Cambridge.
February, 1925.

CXX. *On the use of Monochromatic X-Rays in the production of Laue Diagrams, and on the Structure of Mother-of-Pearl.* *By* J. H. SHAXBY, *D.Sc.*, *F.Inst.P.* *

[Plate XIII.]

THE usual pattern of Laue spots, produced by a high-tension source generating a continuous X-ray spectrum, presents certain difficulties of interpretation, as the position of a given spot depends on two unknown quantities, the architecture of the crystal and the wave-length of the ray forming the spot. If, on the other hand, monochromatic X-rays are employed, of known wave-length, the number of spots is so much reduced that in many cases little information can be drawn from the pattern as to the crystal structure. In some cases, however, the number of spots is sufficient and interpretation then becomes simple, because the wave-length is definite and known. If the tension across the tube is not too great, and if the crystal is thin or its atoms are of comparatively low atomic number, its transparency to the K-rays of the anticathode renders the effective wave-length that of the K doublet; the continuous spectrum plays a negligible part. If, on the other hand, the crystal is strongly absorptive or a subsidiary filter is introduced, the K rays become quite subordinate to the filtered residue of the continuous spectrum. The transmitted beam in this case is still approximately monochromatic and is of wave-length a little longer than the quantum limit corresponding to the tension employed. Its effective value can be determined spectrographically or by calculation from the known absorption coefficients of the crystal (or subsidiary filter). This wave-length is now independent of the material of the anticathode, for instance, in the experiments described below the pattern obtained was the same with anticathodes of silver and of tantalum, under the same tension, 40 kilovolts.

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* Communicated by the Author.

I have carried out experiments of this nature in determining the structure of mother-of-pearl (nacre), using the apparatus excited at constant tension described by Dr. A. Dauvillier *, consisting of a motor-generator supplying alternating current of 600 cycles per second, used in connexion with a high tension transformer and pairs of condensers and kenotrons. The apparatus thus provides current which, at a tension of 40 kilovolts, is constant to within 1 per cent.

The tube is of quartz and is about 2 inches in diameter; the anticathode, fitted with a screwed-in and readily changed target, is water-cooled, and the thin celluloid window is likewise cooled by an air blast. The cathode hot wire of tungsten is supplied with 3·0 to 3·75 amperes, and the cathode is earthed through a high-frequency choke. The tube when in operation was connected to a glass condensation pump, backed by a Gaede pump, the initial vacuum being obtained by a rotary oil-pump.

In most of the experiments with mother-of-pearl the tube was fitted with a silver target and was run at a tension of 40

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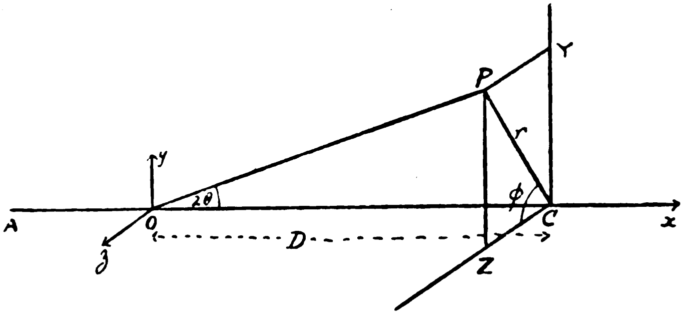
* *Jour. de Physique*, iii. p. 154 (1922).

kilovolts; with about 20 milliamperes an exposure of 4 hours was sufficient for specimens 1 cm. thick.

In investigating a method of differentiating natural pearls (perles accidentelles) from the Japanese artificial pearls (perles de culture Japonaise), Dauvillier [*] found that mother-of-pearl gave diffuse Laue spots. With certain orientations of the specimen (incident beam normal to the laminations of the substance) 6 spots appear in a more or less regular hexagonal pattern, while with others (beam parallel to laminations) a considerable number of spots appear, approximately in a rectangular formation.

To improve the definition of the spots as far as possible in the present series of measurements, a tubular collimator was mounted inside the X-ray bulb [†] and a lead block pierced with a small hole was mounted a few centimetres in front of the window. The specimens were affixed to this block over the aperture and the narrow pencil of rays thus defined produced the Laue pattern upon a photographic plate set up about 11 cm. beyond the nacre. The spots were sufficiently sharp to permit their distances from the central spot to be measured with an accuracy of about 2 per cent.



(2) Let AO be the narrow incident pencil of X-rays falling upon a diffracting crystal placed at O, the origin of coordinates. Let C be the position of the central undiffracted spot, P that of a Laue spot. Let OC = D, and let θ be the grazing angle for the set of atomic planes which give rise to the spot P, so that the angle COP $= 2\theta$. Let angle PCZ $= \phi$.

Then, if l, m, n, are the direction cosines of the normal to the planes of atoms considered, it is clear that

$$l = -\sin\theta\,;\quad m = \cos\theta\sin\phi\,:\quad n = \cos\theta\cos\phi.$$

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[*] *C. R.* clxxix. p. 819 (1924); *Jour. de Physique*, p. 123 (1924).

[†] The tube is essentially that figured at p. 85 of 'La Technique des Rayons X': Dauvillier (*Conf. Rapp. sur la Physique*, Paris, 1925).

If we call l', m', n' the direction cosines of the normal to the planes producing a second spot, and ψ the angle between the two normals,

$$\begin{aligned}\cos\psi = ll' + mm' + nn' &= \sin\theta\sin\theta' \\ &\quad + \cos\theta\cos\theta'(\sin\phi\sin\phi' + \cos\phi\cos\phi') \\ &= \cos\theta\cos\theta'\cos(\phi-\phi') + \sin\theta\sin\theta'.\end{aligned}$$

Hence if the Laue spots are near C, so that θ and θ' are small, $\psi = (\phi-\phi')$, or the angle between the radii drawn from C to the two spots is equal to the angle between the two sets of planes responsible for the two spots.

Also the distance d between consecutive atomic planes giving rise to a Laue spot is equal to $\lambda/2\sin\theta$ (θ being known from the equation $r = \mathrm{D}\tan 2\theta$, where r is the distance of the spot from C), and d is practically the distance between the neighbouring principal planes perpendicular to plane yz in the direction specified by ϕ. Thus the distribution of atoms in the yz plane is known.

Plate XIII. shows the general form of the Laue pattern when the incident X-rays are parallel to the laminations of the specimen of mother-of-pearl. In the case shown the plane perpendicular to the rays is the (100) plane, the diagram when they are normal to the (010) plane is essentially similar, with altered values of ϕ and r. When the rays are incident normally to the laminations the symmetry is sixfold, and the spots are very diffuse *.

3. Chemical analyses of nacre † show that it consists of calcium carbonate (75 per cent. to 90 per cent.), organic material, chiefly conchyolin, and water. The relative proportions of the two latter constituents are very variously stated. This composition is thus very similar to that of true pearl, which contains about 92 per cent. of calcium carbonate and 4 per cent. or 5 per cent. of conchyolin ‡. The organic matter appears to form a meshed or honeycomb structure, in the cells of which the mineral substance is deposited as minute crystals, by migratory calciferous cells §. In the pearl the conchyolin alveoli form a radial framework, so the pearl is built up of concentric shells, like the coats of an onion.

The cells in which the calcium carbonate is deposited are of optical dimensions, of the order of 1 μ, and this structure

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* *C. R.* clxxix. p. 1602 (1924).

† L. Boutan, *Bull. de la Station biol. d'Arcachon* (1921).

‡ G. & H. Harley, Proc. R. S. xxiii. p. 461 (1888).

§ R. Dubois, *C. R.* cxxxviii. p. 710 (1904).

is responsible for the lustre and iridescence of pearls and nacre.

The calcium carbonate is in the form of aragonite. The atomic structure of this mineral has been the subject of an *a priori* study by Huggins *, and radiometric measurement by W. L. Bragg †. Aragonite crystallizes in the orthorhombic system and possesses a quasi-hexagonal symmetry about the *c*-axis. The three axes are in the ratios, $a : b : c = 0{\cdot}623 : 1 : 0{\cdot}720$ ‡.

Huggins concluded that $a = 3{\cdot}930$ Å, $b = 6{\cdot}310$ Å, and $c = 4{\cdot}546$ Å, and that the unit of crystalline structure contains $2(CaCO_3)$. Bragg's experiments led him to ascribe aragonite to the holosymmetric class of the orthorhombic system, with a crystalline unit containing $4(CaCO_3)$. The three axes are of lengths 4·94 Å, 7·94 Å, and 5·72 Å, and the arrangement of atoms is quite different from that supposed by Huggins.

4. The measurements I have made with mother-of-pearl entirely confirm Bragg's model. It will suffice to quote the results of the measurements of plates furnished by rays parallel to the laminations of the nacre and approximately in the (100) and in the (010) directions. (Tables I and II.)

TABLE I.

Effective wave-length 0·40 Å.

Observed ϕ°.	Calculated.	Observed d(Å).	Calculated.
0	0	2·42	2·49
22·5	23·4	2·26	2·265
38	40·9	3·53	3·385
57	60·0	2·41	2·47
68	68·9	1·76	1·77
90	90	2·90	2·86

TABLE II.

Observed ϕ°.	Calculated.	Observed d(Å).	Calculated.
0	0	3·89	3·97
36	34·8	2·84	2·92
54·5	54·3	4·04	4·11
70	70·2	2·41	2·36

Bragg gives an interesting description and diagram of the common mode of twinning, across the 110 planes. It will be seen that this twinning and the fact that the symmetry about the *c*-axis is pseudo-hexagonal and not perfect—the angles are 58° 8′ and 60° 56′—lead to a changing orientation of those faces which are parallel to the *c*-axis. This produces a sufficient variation in the angle of incidence of the X-rays upon the planes rich in atoms to permit a narrow range of wave-lengths to produce a considerable number of spots. The correct incidence is attained much as in the case of rotating crystals. The quasi-hexagonal *c*-axis retains its direction, hence the effect is not like that of a heterogeneous crystalline powder: the heterogeneity is partial and is further only two-dimensional. With photographs taken by means of rays travelling in the direction of the *c*-axis this change of orientation makes itself felt in the greater diffuseness of the spots and in some cases in their almost complete fusion into a ring, somewhat resembling a solar halo with six mock-suns.

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* Phys. Rev. xix. p. 354 (1922).

† Proc. R. S., A. cv. p. 16 (1924).

‡ Groth, *Chem. Krystallographie*, ii. p. 200.

Mother-of-pearl thus consists, so far as its mineral constituents are concerned, of aragonite crystals whose quasi-hexagonal axes are perpendicular to the planes of lamination.

I wish to express my sincere thanks to M. le Duc de Broglie, in whose laboratory the work was carried out, and to Dr. A. Dauvillier, for much advice and assistance.

Welsh National School of Medicine,
Cardiff.

CXXI. *Emission Band Spectra of Aromatic Compounds. Part II.—Their Origin.* *By* JOSEPH KENNETH MARSH, *D.Sc.*[*]

IN the previous paper[†] it has been shown that in every case which has come under notice of multiple banding in emission spectra there is evident a difference between the successive frequencies amounting to the absolute frequency of a band in the near infra-red absorption spectrum. It therefore seems obvious that the physical significance of the bands in both instances will be similar, and as in the case of the infra-red bands a fairly complete and satisfactory explanation has been arrived at, the way seems open for an extension of the same principles to the regions of higher frequency.

Briefly it may be stated that these infra-red bands are supposed to be due to the quantized vibration of groups of atoms, or molecules. If a disturbance is taking place in a molecule it follows that the forces existing between the atoms are in a state of change. In the case of a diatomic molecule the equilibrium existing between the electrostatic and gravitational forces is disturbed and there results a vibration of the atoms in their line of junction. Absorption bands of the quantum frequency of this vibration are seen in the near infra-red. These, however, are not simple bands but under high dispersion are capable of resolution into series of finer bands at approximately equal intervals, these bands being due to the changes in the rotational energy of the molecule. Further, the pure rotation spectrum may be observed in the far infra-red ($\lambda > 100\mu$). If ν_v is a vibration frequency and ν_r a rotation frequency, in the near infra-red spectrum bands expressible by the formula $\nu_v \pm \nu_r$ will be found. Such bands are known as rotation-vibration bands. The best examples are found in the case of the halogen acids which have been examined by Imes (Astrophysical J. l. p. 251 (1919)). Due to the changes in the moment of inertia during vibration and changes of centrifugal forces during rotation these two motions have mutual effects, which may be observed in the spectra. The rotation-vibration bands are caused to be bunched together towards the high frequency end instead of being evenly distributed, whilst the overtone vibration bands become shifted to positions rather less than exact whole number multiples of their fundamentals.

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[*] Communicated by the Author.

[†] *Suprà*, p. 971.

Due to the movements of the electrons in their orbits we obtain in the ultra-violet or visible regions absorption or fluorescence spectra of organic compounds. If the frequency due to the electronic jump is ν_e and the molecule is simultaneously emitting or absorbing vibrational and rotational energy at frequencies ν_v and ν_r we may find in the spectrum all the frequencies $\nu_e + m\nu_v \pm n\nu_r$ where m and n are small whole numbers. Further, in a complex molecule there may be more than one type of vibrational motion between the atoms, *i.e.*, there may be more than one term represented by $m\nu_v$.

If the electronic energy is undergoing an increase ν_e should be observed as an absorption band; if a decrease, as an emission band. From the experimental fact that as a general rule absorption and emission do not overlap extensively in the case of organic compounds, but are contiguous, the emission being of lower frequency than the absorption, we may infer that both emission and absorption cannot occur at $\nu_e + m\nu_v$ but only the former, and at $\nu_e - m\nu_v$ only the latter. On this basis the electronic frequency may be said to occur at the boundary between the emission and absorption regions. Further, we may infer that whilst electronic energy is both absorbed and emitted we only have evidence of the absorption of atomic vibrational energy. This is true also in the infra-red, banded emission spectra never having been observed.

We may now turn to a consideration of some individual spectra.

The Spectra of Benzene.

The absorption bands of benzene have been measured with the greatest accuracy by Henri (J. Phys. Rad. iii. 181 (1922)), who found that they could be represented by a formula derived from a consideration of the energy contents of the molecule. In two states the electronic, atomic, and molecular energy will be represented by

$$W_e + W_a + W_m = Bh + phb + \frac{h^2q^2}{8\pi^2 I} \quad . \quad . \quad . \quad (1)$$

$$W_e + W_a + W_m = Ah + nha + \frac{h^2m^2}{8\pi^2 I} \quad . \quad . \quad . \quad (2)$$

The formula representing the observed band systems is

$$\nu = A - B + na - (pb + p^2b') + \alpha(m^2 - q^2), \quad . \quad . \quad (3)$$

which is derivable from 1 and 2 with the exception of the term p^2b', the value of which, however, is very small. The high frequency term A − B in 3 which determines the general region of absorption is electronic in origin. The large band systems such as persist in solution as well as the finer band systems (terms in a and b in 3) are atomic, whilst the finest structure is molecular.

A formula similar to that deduced by Henri is found to fit the fluorescence bands. He divided all the bands observed into four series having different values for the term A − B in 3. Three of these series had $a = 921{\cdot}4$, $b = 152$, $b' = 2$, but the fourth had $b = 166$. $b' = 0$. The electronic and atomic terms of the second of these series are given by the formula

$$\nu = 37494 + 921{\cdot}4\, n - (159p + 2p^2).$$

(*Note.*—these figures represent waves/cms., whereas in the previous paper we have used a unit ten times this size *i.e.*, waves/mm.) This may be written

$$\nu = 37494 + 6n159(1 - {\cdot}0358) - 159{\cdot}2p(1 + {\cdot}01257p) \quad . \quad . \quad (4)$$

All the chief bands in the fluorescence spectrum are well represented by the formula

$$\nu=37494-6n159(1+\cdot0358)-159\cdot2p(1+\cdot01257p), \quad . \quad (5)$$

which differs only from the absorption formula in the matter of signs. In the table below the calculated positions of the chief bands, according to the above formula, are confronted with the observed frequencies.

Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$n=0$.		$n=1$.		$n=2$.	
37494	37490	36504	36510	35514	35520
37335	37340	36345	36350	35355	35360
37174	37170	36184	36180	35194	35200
37007	37000	36017	—	35027	35040
36830	36830	35840	35860	34850	34870?
36639	36630	35749	35750		
$n=3$.		$n=4$.		$n=5$.	
34524	34530	33534	33540	32544	32540
34365	34360	33375	33370	32385	32370
34204	—	33214	—	32224	32220
34037	34050	33047	—	32057	32040
34860	34890-770	32880	32880		

The correcting factors $\cdot01257p$ in the last term of 4 and 5 corresponds to what is found to be required for the expression of the successive overtone bands of a rotation-vibration spectrum to make allowance for the effect of the rotation on the vibration. This points to the benzene bands being successive overtones of a band of frequency 159, and to their having the same physical significance as rotation-vibration spectra.

The features of the benzene spectrum which it is desirable to explain are (1) the recurrence of bands at intervals of 159 units; (2) the recurrence of bands at intervals of 921·4 or 987 units; (3) the cause of the difference of this interval in the case of absorption and emission; (4) the cause of the difference of the most refrangible band from the others, and of the double or triple heads observed in the other bands.

The Kekulé formula for benzene represents it as a condensation of three molecules of ethylene, and as the infra-red spectrum will have to be considered parallel with the ultra-violet, we shall start by examining the infra-red spectrum of ethylene. (See diagram in previous paper.) The four outstanding bands are:—

No. ……	1	2	3	4	(5	
λ ………	3·28	5·3	6·98	10·5	21·0	
ν ………	3049	1887	1433	952·4	476)	
Diff. …..		—	454	481	476	476

Nos. 2, 3, and 4 are obviously overtones of a band (No. 5) at about $21\,\mu$, ν 476 which is beyond the limit to which measurements have been carried. No. 1 does not belong to the same series. Thus characteristic of ethylene are bands at intervals of 476 units, multiples of an hypothetical fundamental of this frequency. Now this value is just three times the interval 159 found for the absorption and emission bands of benzene. It appears then that the spectrum of benzene is derived from that of ethylene, but concurrently with the condensation of the three ethylene bands together a diminution of the ethylene frequency to $\frac{1}{3}$ of its normal value takes place. The frequency of the ethylene band No. 1 will likely be affected similarly, and we must therefore look for a strong benzene band at $3{\cdot}28 \times 3$, *i. e.*, $9{\cdot}84\,\mu$. Actually the strongest band of benzene is found at $9{\cdot}8\,\mu$. Thus we find ethylene has two characteristic frequencies 3049 and 476, and in benzene both these are reduced to $\frac{1}{3}$ the value, 1020 and 159. The question now arises as to what influence the frequency 1020 has on the absorption and emission spectra of benzene. Considering first the emission spectrum we have regarded the position $\nu = 37494$ as the zero point, *i. e.*, the electronic frequency. By subtracting from this successive multiples of 159 we get the series of bands forming the first (F) group (See Pl. X.*). At 36474 we might expect a band due to the frequency 1020 and at 37540 the sixth multiple of the 159 series. There might also be a third band mid-way between these two due to their cooperative effect, Actually all three are seen. A faint band corresponding to the 6th multiple of 159 occurs in front of the head of band E. The strong head is double, consisting of two components $37494 - \frac{(1020+954)}{2}$ and $37494 - 1020$. Subsequent bands of group E have frequencies approximately $159n$ less than one or other of these two bands. Taking the head of E as a new zero point we should have for the head of D frequencies $(1020+954)/2$ and 1020 less, but the head of Group E being itself double we obtain three strong bands in Group D for every one seen in F. Further, the multiples of 159 have successively less influence with the 2nd, 3rd, and 4th multiples of 1020, so that there is a gradual transition of the interval between the strongest bands to 1020 units, but meanwhile the spectrum becomes very indistinct. A subsidiary system of bands occurs at intervals of 159·2. In the benzene emission spectrum we have usually taken the larger periodicity as 987, which is a mean between 954 and 1020, and the whole spectrum is explicable as a resultant of two vibrations 1020 and 159. In the absorption spectrum the periodicity is decreased below 954 by exactly the same amount as in emission it is increased above this figure, and periodicities of 921 and 159 are found (Henri, *loc. cit.*) ; 954 or 6 × 159 is therefore the mean of the absorption and fluorescence values.

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* Phil. Mag. May 1925.

The main features of the benzene spectra are explicable as resulting from the compounding of two infra-red frequencies. Of these the smaller appears to be characteristic of ethylenic compounds *i.e.*, of the C=C linkage, but the larger differs but slightly from the ordinary value of a vibration common to all compounds with CH groups. Benzene and its derivatives have a band at about 3·25 μ, whilst in aliphatic compounds it is found at about 3·43 μ. To obtain the interval found in the benzene spectrum (1020) the frequency of this band (3077) must be divided by the factor 3. With other substances other factors may be required. Thus the intervals of about 400, 750—800, or 1600 units found in the aliphatic substituted type of spectrum may be regarded as eighths, quarters, or halves of the 3·25 region frequency. This band should therefore be at least the 24th multiple of a fundamental which will have a frequency of 128·25. Most of the infra-red absorption maxima considered by Coblentz as characteristic of benzene are found to be accurately expressed as multiples of such a frequency. This will be seen from columns 2 and 3 of the following table, though the correspondence of the higher multiples is less exact than of the lower, probably due to the accumulation of the small rotational effects previously mentioned. The band at 11·8 μ is seen to have an independent origin. In the last column the positions of the bands which Coblentz considered characteristic of CH_2 or CH_3 groups are given for the purpose of comparison with the position of a parallel series in benzene. There can be little doubt that both these series have their origin in CH vibrations but that the frequency is somewhat raised in benzene and derivatives. The raising of the frequency means that there is more energy in the CH bond or that the H is bound tighter when the carbon atom to which it is attached has a large amount of unsatisfied valency. From the study of the infra-red absorption spectrum of acetylene made by Coblentz it can be seen that a triple bond has an even more pronounced effect. He found the corresponding band at 3·08 μ in this case. The following examples demonstrate the effect admirably.

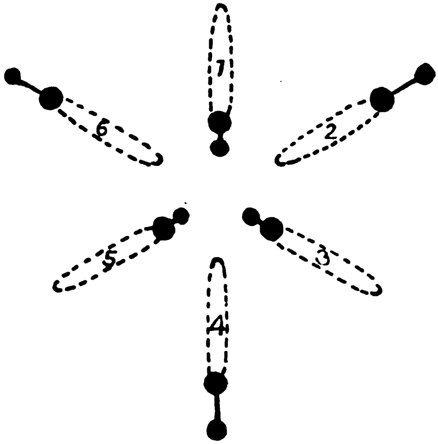
Acetylene	$HC\equiv CH$	3·08 μ.
Ethylene	$H_2C=CH_2$	3·28 μ.
Ethane	H_3C-CH_3	3·39 μ.

The value for higher aliphatic hydrocarbons further rises slightly to a constant value of 3·43 or 3·44μ with chains of five or six carbon atoms, suggesting that with the completion of an open ring a satisfaction of part of the residual affinity of carbon is attained. In the case of the isomeric xylenes it is found that when the CH_3 groups are far apart the benzene band at 13μ is not disturbed, but when they approach to the ortho position the band is found at 13·6μ, or nearly the normal position for aliphatic compounds.

Characteristic Infra-Red bands of Benzene as multiples of ν 128·25.			Characteristic Aliphatic CH Bands.
Multiple.	*Calculated.*	*Observed.*	
	ν	ν	ν
6	13·0	12·95	13·6–13·8
		11·8	
8	9·75	9·78	
9	8·67	8·67	
12	6·50	6·75	6·86
24	3·25	3·25	3·43
32	2·44	2·49	
36	2·17	2·18	
48	1·63	1·68	1·71
96	·813	·84	·86

From the point of view of the mechanism of the benzene molecule it is interesting, now that we have established the connexion of the benzene bands at intervals of 159 units with the vibration between carbon atoms, to note again that these bands show evidence that the atoms originating them are in a state of rotation with regard to one another. This must mean that the carbon atoms in the molecule circulate in orbits so that their distances from the centre of the molecule will vary. Carbon atoms 1 and 2 are at extreme phases of such orbits in the accompanying diagram (p. 1213).

The recent analysis of the band at 3·25μ in benzene by Meyer and Bronk (Phys. Rev. 1923, xxi. p. 712) into bands at $1/\lambda$ 3093·0, 3050·3 and 2965·4, showing intervals of 42·7 and 84·9, suggests that here we have direct evidence of the rotation of CH groups. The moment of inertia of a system giving an interval of 42·5, assuming it to have one quantum of rotational energy, will be $1{\cdot}31 \times 10^{-40}$, which is very near the values found for HF or H_2O on the same assumption. The CH vibration in the case of the benzene molecule appears to be an integral multiple of the CH rotation frequency. Thus the rotation bands of Meyer and Bronk are at intervals almost exactly $\frac{1}{3}$ and $\frac{2}{3}$ the magnitude of the fundamental vibration 128·25, but for the characteristic CH bands six times this fundamental would be a small enough basic unit, and the rotation frequency would then be a correspondingly smaller fraction of the vibration frequency. That such a relationship should exist seems not at all unlikely. All we have to postulate is that when the carbon atoms are in one or other of their extreme phases as regards distance from the centre of the molecule the CH rotation and vibration are also in extreme phases. We have tried to represent a possible system of this sort in the diagram. The hydrogen of atom 1 is shown at extreme proximity to carbon, and in atom 2 at extreme remoteness, while the CH rotation has undergone half a revolution.



There may have been several CH rotations or vibrations during the epoch in which the carbon atom has undergone the translational change of phase indicated, but at least it seems only reasonable, if symmetry is to be preserved, to suppose that a whole number and one-half of such rotations and vibrations have taken place. There must then be a simple numerical relationship between the two frequencies.

It will not be necessary to deal in detail with the aliphatic hydrocarbon derivatives of benzene. In the preceeding paper it have been shown that the spectra are generally a mixture of types which we may now term the C=C and C–H varieties.

Naphthalene and Anthracene Spectra.

Both ultra-violet absorption and fluorescence of naphthalene exhibit long series of bands at 474 unit intervals. This shows that the spectrum is of the C=C or ethylene type, and little trace of CH influence can be found.

Anthracene bands are at intervals of 1420 or 3 × 473 and therefore of the same type, but the spectrum is much less sharp than with benzene or naphthalene. It will be noticed that each stage in the condensation of nuclei has produced a three-fold increase in the frequency connected with the double bond. In condensing ethylenic groups to benzene a three-fold decrease occurs. This may be paralleled with the chemical reactivity of the double bond which is of course greatly modified in the case of benzene. But on increasing the number of conjugated bonds as in naphthalene and anthracene the frequency again rises, and to some extent the character of the ethylene bond is restored, *e.g.* naphthalene and anthracene are more readily hydrogenated or halogenated than benzene.

The C = O Vibration.

It has been found that substances which give the strongest "blue bands" contain a CO group, though the converse is not true. No emission spectrum has been detected from salicylic or cinnamyl aldehydes whilst methyl salicylate gave a perfectly continuous spectrum. The view of Coblentz with regard to the origin of the corresponding infra-red band at or about 5·8μ is that "it is not to be found except in those substances containing a CH_3 group and in benzaldehyde. Whether this band is due to CH_3 or some other group vibrating like a CH_3 group is a pertinent question." Examination of the work of Coblentz, however, will show that it is entirely absent in ethane, and it is never strong in aliphatic hydrocarbons, though it certainly does often appear as a minor band. On the other hand it is the strongest band in the acetone spectrum, and is always strong in the aliphatic acids of which a considerable number were examined, and is strong also in the two esters investigated. Among aromatic substances it is very strong in benzaldehyde and cuminol, the only two aldehydes examined. It is also strong in benzoic acid (Spence, Astrophysical Jour. xxxix. p. 243. (1914)) and in phenyl acetic acid. Traces of it were found in other aromatic substances, notably eucalyptol and safrol. It will be seen that whilst Coblentz' statement is correct it appears more reasonable to consider the carbonyl group as the most powerful influence making for the production of this band. Further evidence pointing to this conclusion may be drawn from the work of Spence (*loc. cit.*), who made a study of the infra-red absorption spectra of certain alkaloids. He found this 5·8μ band in a number of instances, whilst it was definitely absent in others. Examples of these classes are given below.

Strong infra-red band at $5{\cdot}8\mu$.	*No Infra-red band at* $5{\cdot}8\mu$.
Pilocarpine.	Nicotine.
Atropine.	Quinine.
Cocaine.	Quinoline.
Homatropine.	Codeine.
Narcotine.	Cinchonidine.

All the alkaloids in the list showing the band contain a CO group, whilst none of the substances in the other list have such a group. This is strong evidence that this band in the infra-red is closely connected with the presence of a CO group.

An observation made in an experiment on benzene is also of interest in this connexion. When the vapour of benzene-alcohol mixtures was submitted to the Tesla discharge blue bands were observed, but benzene alone did not give them. The explanation would seemingly be that with alcohol present there is introduced a source of oxygen which under the influence of the Tesla discharge may react to give compounds having a blue band spectrum.

As both in the infra-red and Tesla spectra substances which *should* contain no oxygen have been found to give to a greater or less extent the $5{\cdot}8\mu$ or "blue bands" it is, perhaps, premature to state dogmatically that these bands have a CO origin, though this is the belief of the writer *. Three classes of vibrations producing banded spectra will then be recognised, due respectively to CH, $C=C$, and CO bonds.

In conclusion I desire to express my best thanks to all those with whom I have been in collaboration in the previous work, which has here been under review, and more especially to Prof. A. W. Stewart and Mr. W. H. McVicker, whose initiative and skill have been larger contributions to it than my own.

Abstract.

From a consideration of a parallel between the infra-red band intervals of ethylene and the ultra-violet band intervals of benzene, naphthalene, and anthracene, the bands exhibited by these substances are considered to originate in a $C=C$ bond. Similarly the band intervals of type (2) of the preceding paper are shown to originate in a CH bond.

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* After very careful purification several of the anomalous substances have now been found to lose all trace of a blue band spectrum.

Benzene also shows vibrations having this origin, and the spectrum is accounted for as a combination of C=C and CH vibrations. It is considered most probable that the "blue band" type of spectrum originates from a carbon-oxygen bond and evidence on this point is brought forward. A view of the benzene molecule is taken accounting for the fact that the bands originating from the two carbon atoms of the C=C bonds show evidence of their being in a state of mutual rotation, whilst the CH groups appear to have a rotation frequency of which their vibration frequency is an exact multiple. This is necessitated if the symmetry of the molecule is to be preserved.

CXXII. *On the Polarization of the Light scattered by Organic Vapours.* *By* A. S. Ganesan, *M.A.**

1. *Introduction.*

It is well known that the imperfection of polarization of the light scattered by gases and vapours observed in a direction perpendicular to the incident beam largely depends on the nature of the scattering substance. For example, in the case of the monatomic gases, argon and mercury vapour, the transversely scattered light is almost perfectly polarized†; in the case of hydrogen the imperfection of polarization, as measured by ρ, the ratio of the weak component to the strong component in the scattered light, is 3·8 per cent.‡, and for carbon dioxide it is 11 per cent.‡. It is not, however, in general, true that the imperfection would increase with the number of atoms in the molecule; for it is found that in the vapour of ether or pentane, whose molecules contain 15 and 17 atoms respectively, ρ is only about 3 per cent., while in the case of the tri-atomic carbon disulphide it is as great as 16·7 per cent. In order to clear up the problem of the relation that exists between the polarization of the scattered light and the structure of the molecule, it was felt that it would be useful to make a systematic study of the scattering by a series of closely related compounds. In this paper are given the results of experiments made on the vapours of the following series of organic compounds:—the paraffins, some monohydric alcohols, the chlorine substitution products of methane, benzene and its derivatives, some esters like formates and acetates, and the ketones.

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* Communicated by Prof. C. V. Raman, F.R.S.

† Lord Rayleigh, Proc. Roy. Soc. xcviii. p. 64; cii. p. 190.

‡ *Ibid.* Raman & Rao, Phil. Mag. xlvi. p. 433 (1923). Cabannes & Granier, *Journ. de Phys.* iv. No. 12, p. 429.

2. *Experimental Arrangements.*

The vapour was contained in an iron cross-tube similar to the one used by Lord Rayleigh and subsequent experimenters, but of more ample dimensions, the inner diameter of the tube being 8 cm. The three short arms, measuring 30 cm. each, were fitted with plane glass windows placed between asbestos rings and held tight by screw-caps. The fourth arm, which was 60 cm. long, was closed at the farther end and contained an obliquely placed green-glass bottle (with its bottom cut off) which formed an efficient background reflecting no light towards the centre of the cross. Sunlight concentrated as described below was admitted through one of the windows, and the scattered light was observed in a perpendicular direction through the other against the black background. At the end of the exit arm was placed a black combination of several colour-filters inclined at 45° so that no light was reflected back. This combination though black was transparent enough to show the direction of the incident beam, which was always kept steady. Apertures of about 3 cm. diameter were placed along the arms at convenient places so as to cut off all stray light. The tube was fairly air-tight, and since in the experiment a continuous stream of vapour was kept passing, it was not found necessary that it should be perfectly air-tight. The cross-tube was wrapped up in a layer of asbestos sheet over which was uniformly wound a coil of nichrome wire which carried a current. The tube could thus be electrically heated and maintained at any desired temperature.

As pointed out by Lord Rayleigh, there was some difficulty regarding the blackening of the interior of the cross-tube. A preliminary experiment was conducted with no painting, but the track was so unsatisfactory that reliable measurements could not be made. Several paints were tried, but some of them were acted upon by the organic vapours, while the others did not stand a high temperature. Finally, the following method was found to satisfy the requirements. The inside of the tube was coated with a solution of sulphur in turpentine and heated with the burner till all the turpentine had evaporated. A smooth black coating of iron sulphide was formed which was not acted upon by the organic vapours.

The three conditions that are necessary to make the scattering by gases and vapours a conspicuous phenomenon, and to render visual observations to be made accurately, are: (1) an intense source of illumination, (2) a perfectly black background, and (3) an arrangement to shield the observer's eyes from all extraneous light.

The objective of an astronomical telescope of 18 cm. aperture and 200 cm. focal length was fed with sunlight reflected from a large plate-glass mirror. An auxiliary lens of 30 cm. focal length, placed beyond the focus of the object-glass and close to the entrance arm of the cross-tube, focussed the light at the centre of the tube. An intense beam of illumination was thus secured. The observer located himself in a light-tight wooden cage of 4 feet square and 8 feet high. In one of the walls of the cage and at the same vertical height as the centre of the cross-tube was an aperture of about 4 cm. diameter through which the illuminated track could be viewed.

The imperfection of polarization was measured with a double-image prism and nicol. The prism was placed between the observation window of the cross-tube and the aperture of the cage, and adjusted to give two images of the illuminated track in the same horizontal line and just side by side with each other. The stronger track corresponds to vibrations perpendicular to both the incident and scattered beams, while the weaker track corresponds to vibrations parallel to the incident beam. The ratio (ρ) between the intensities of these two components (which is a measure of the polarization of the scattered light) was determined by means of a nicol which could be rotated and whose position could be read on a graduated circle. The combination of the nicol and the graduated circle was fixed inside the observer's cage at the aperture in the wall. The two positions of the nicol for which the two tracks were of the same intensity were found, and if the angle between these two positions be denoted by 2θ then ρ is given by $\tan^2\theta$. The double-image prism was enclosed in a long black cylindrical tube leading from the cross-tube to the aperture. The tube was covered with several layers of black cloth to make it light-tight. With these arrangements the observer could see only the two tracks and visual observations could be made with a high degree of accuracy.

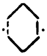
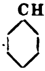
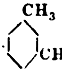
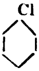
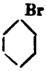
3. *Supply of Vapour and Procedure.*

For accurate work it is essential that the vapour must be pure and free from dust. In all cases Kahlbaum's chemicals were used. The liquid was evaporated from a glass retort and the vapour was made dust-free by passage through a tube packed with clean, dry cotton-wool. The tube was electrically heated and maintained at the temperature of the cross-tube by passing a current through a coil of nichrome wire wound round it. The cross-tube was previously made dust-free and heated to a temperature slightly above the boiling-point of the liquid whose vapour was under investigation. When the vapour had passed through for about fifteen minutes it drove away all the air, and the scattering by the pure vapour was observed. The track was well-defined and intense, and measurements were made only when it had been ascertained that there was no dust or formation of clouds. Any tendency to develop a cloud under the action of light could easily be detected. The track instead of being blue became distinctly white, and in some cases was of a streaky nature; the readings showed wide variations with time. In such cases the difficulty was overcome by limiting the illumination to just the time necessary to take a reading. In each case more than 30 readings were taken. After experimenting with each vapour, the cross-tube was heated to a high temperature and a strong blast of filtered air was passed through for about half an hour till all the vapour had been removed. The retort was thoroughly cleaned and dried and the cotton plug was renewed.

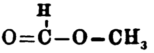
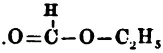
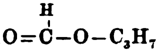
4. *Experimental Results.*

Substance.	Formula.	$\frac{\text{Intensity of weak component}}{\text{Intensity of strong component}}$ in per cent.
The Paraffins and unsaturated Hydro-carbons.		
Pentane	$CH_3 . CH_2 . CH_2 . CH_2 . CH_3$	3·4
Hexane	$CH_3 . CH_2 . CH_2 . CH_2 . CH_2 . CH_3$	3·3
Heptane	$CH_3 . CH_2 . CH_2 . CH_2 . CH_2 . CH_2 . CH_3$	3·1
Octane	$CH_3 . CH_2 . CH_2 . CH_2 . CH_2 . CH_2 . CH_2 . CH_3$	2·7
β-iso-amylene (trimethylethylene)	$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CH . CH_3$	6·1
Alcohols.		
Methyl alcohol	$CH_3 . OH$	2·7
Ethyl alcohol	$CH_3 . CH_2 . OH$	1·7
n. Propyl alcohol	$CH_3 . CH_2 . CH_2 . OH$	2·0
Iso-Propyl alcohol	$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH . OH$	1·9
n. Butyl alcohol	$CH_3 . CH_2 . CH_2 . CH_2 . OH$	2·8
Iso-Butyl alcohol	$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH . CH_2 . OH$	1·8
Allyl alcohol	$CH_2=CH . CH_2 . OH$	5·2

Benzene and its derivatives.

Benzene		6·6
Toluene		6·4
Meta-Xylene		6·7
Chloro-benzene		7·8
Bromo-benzene		7·8

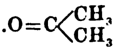
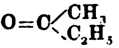
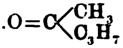
Formates and Acetates.

Methyl-formate	 $O=\overset{H}{C}-O-CH_3$	4·6
Ethyl-formate	 $O=\overset{H}{C}-O-C_2H_5$	3·3
Propyl-formate	 $O=\overset{H}{C}-O-C_3H_7$	3·5
Methyl-acetate	$CH_3.CO.O.CH_3$	4·8
Ethyl-acetate	$CH_3.CO.O.C_2H_5$	3·4
Propyl-acetate	$CH_3.CO.O.C_3H_7$	3·2

Chlorine substitution products of Methane.

Chloroform	$CHCl_3$	3·2
Carbon tetrachloride	CCl_4	1·9

Ketones.

Dimethyl ketone	 $O=C\begin{matrix}CH_3\\CH_3\end{matrix}$	4·8
Methyl-ethyl ketone	 $O=C\begin{matrix}CH_3\\C_2H_5\end{matrix}$	4·4
Methyl-propyl ketone	 $O=C\begin{matrix}CH_3\\C_3H_7\end{matrix}$	3·2

Carbon disulphide	$S=C=S$	16·7
Ether	$C_2H_5-O-C_2H_5$	3·2

5. *Comparison with previous measurements.*

ρ expressed as a percentage.

Substance.	Rayleigh *.	Raman and Rao †.	Author.
Pentane ‡	1·2	2·8	3·4
Benzene	6·0	6·8	6·6
Chloroform	3·0	3·0	3·2
Carbon tetrachloride.	3·5	3·2	1·9
Carbon disulphide	12·0	—	16·7
Ether	1·7	3·0	3 2

6. *Discussion of Results.*

At this stage it is perhaps premature to attempt a detailed discussion of the relation between the structure of the molecule and the polarization of the light scattered by it. Experiments have also been made on the scattering of light in organic liquids by Mr. K. S. Krishnan in this laboratory, and when these data have been published it is proposed, in a joint paper, to discuss the problem in detail. But based on the experimental values quoted above, some outstanding facts may be mentioned.

In the paraffin series of compounds, as we pass from pentane to octane, the molecules become longer, and if we associate optical anisotropy with anisotropy of shape, we might expect an increasing optical anisotropy as we go up the series. But from the values given above, it is clear that there is no such increase in the depolarization ; if anything, there is a tendency for an actual decrease in the value.

Another interesting fact is that whenever we have a "double bond" in the structure of the molecule, we have a high value for the "factor of depolarization." This is to be seen in the case of the unsaturated hydro-carbon amylene, which has a value nearly twice that for the paraffin series ; and also in the case of allyl alcohol, where the depolarization is much greater than for the mono-hydric alcohols. The iso-compounds show a smaller optical anisotropy than the normal ones.

The benzene series affords a very interesting study. The three homologues benzene, toluene, and xylene show the same degree of imperfection, namely 6·5 per cent. This may be explained as due to the predominating influence of the closed chain of the six carbon atoms, the hydrogen or its substitution by an alkyl radicle exerting little or no influence on the optical anisotropy of the molecule.

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* Strutt, Proc. Roy. Soc. xcv. p. 155.

† Phil. Mag. xlv. (March 1923) ; xlvi. (Sept. 1923).

‡ R. Venkateswaran, Trans. Chem. Soc. cxxi. p. 2655 (1922).

The methyl compounds always show a greater imperfection of polarization than the ethyl ones. This is to be seen not only with the formates, acetates, and alcohols but also with the ketones, where dimethyl ketone containing two methyl radicles shows a greater value for ρ than the other two compounds.

As is to be expected, the more symmetrical molecule CCl_4 shows a smaller value for ρ than chloroform $CHCl_3$. Experiments are in progress to investigate the effect of successive replacements of H by Cl in CH_4.

In conclusion, I have much pleasure in recording my indebtedness to Professor C. V. Raman for the great interest he took in the experiments, which were conducted at the Physical Laboratory of the Indian Association for the Cultivation of Science.

Calcutta,
26th June, 1924.

CXXIII. *On some Chemical Deposits of a Regular Form.*

By J. M. MULLALY, *B.A.*, *War Memorial Student in Natural Science, Balliol College, Oxford* *.

THE deposits are those of the salt ammonium chloride obtained by the steady diffusion through one another of ammonia and hydrogen chloride in a glass tube of uniform bore. A medium of air was present in the tube.

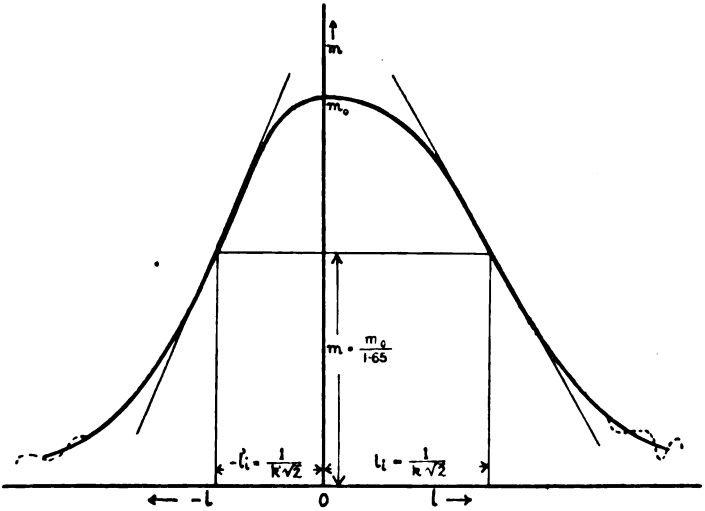
The object has been to find experimentally the law of distribution of deposit along the axis of the tube, that is, to find the curve representing the mass of salt condensed in a given time per unit area of the tube wall at different points.

The means employed was the direct estimation of thickness by means of a travelling microscope focussed on the crystals from the exterior, and radially to the walls, which have been cleared of deposit on the nearer side. Refraction by the glass did not, of course, distort the deposits in the line of the axis. The precision attained was sufficient on a thickness of 0·1 to 2 mm.

* Communicated by the Author.

It would seem that the distribution may be represented by the combination of two error curves, with a common origin at the point on the axis where the deposit is thickest.

Let the axis be regarded as positive on the side from which ammonia diffuses, and negative on that from which the hydrogen chloride diffuses.



Then the curves are

$$m/m_0 = e^{-k^2 l^2} \text{ in the positive region,}$$

and

$$m/m_0 = e^{-k'^2 l^2} \text{ in the negative region.}$$

k and k' are constants in a given tube. m_0 is the maximum value of m where $l = 0$.

The curves terminate at the sources of the two combining gases, and thus extend over a region fixed arbitrarily by the positions of these sources upon the axis.

The experiments were as follows :—

l. in mm.	Thickness in mm.	$k^2 = -\frac{2·303}{l^2}\log_{10}\frac{m}{m_0}$ in mm.$^{-2}$.
0·	1·20 (m_0)	
0·25	1·13	0·50
0·50	1·08	0·45
0·75	0·89	0·53
1·00	0·73	0·50
1·50	0·37	0·46
2·00	0·19	0·52

To determine k (or similarly k') it is most convenient to locate upon the axis of the tube the corresponding point l_i of inflexion at which

$$\frac{d^2m}{dl^2} = -2m_0k^2e^{-k^2l^2}(1-2k^2l^2)=0.$$

Hence $$1-2k^2l_i^2=0,$$

or $$k=\frac{1}{l_i\sqrt{2}};$$

similarly $$k'=\frac{1}{l_i'\sqrt{2}},$$

where l_i' locates the point of inflexion in the negative region. Negative values of k and k' are inadmissible.

The points of inflexion can readily be seen without optical aid; and occur where $m=\frac{m_0}{\sqrt{e}}=\frac{m_0}{1{\cdot}65}$.

As the deposit grows from moment to moment, the values of k and k' do not change. Again, other things being equal, these constants are unchanged whether the tube be narrow or whether it be wider, if not much exceeding the usual quill size.

The magnitudes of k and k' for a given length of tube may vary within extremely wide limits according to the temperature and other circumstances, *e. g.* the nature of the sources of the vapours. But such circumstances are here considered alike for all the tubes.

For comparison of various tubes, k and k' may well be referred to the respective distances L and L$'$ of the two sources (ammonia and hydrogen chloride) from the origin.

Tube.	L.	L$'$.	k.	k'.	kL.	k'L$'$.
	in mm.		in mm.$^{-1}$.			
1 ……	770	−256	0·7	1·0	540	−256
2 ……	369	−127	1·6	2·1	590	−266
3 ……	670	−218	0·9	1·2	600	−262

It is evident that kL and $-k'$L$'$ are numerical constants having the values 560 and 260 under the chosen circumstances. This indicates the fact that $\frac{l_i}{L}$ and $\frac{l_i'}{L'}$ are constants under the given conditions, which is easily imagined since the diffusion occurs in a steady state.

As sources of the gases aqueous hydrochloric acid of 7·7 N strength, and ammonium hydroxide of 0·49 N strength, were used, being chosen somewhat at random. The tubes were kept at a temperature of 25°·0 C. in a thermostat.

A stream of water vapour diffused through these tubes from the side containing ammonia to that containing the acid. This does not cause a change in the form of the law, though it influences the values of the constants.

It might be mentioned that in the outer fringes of the deposits were sometimes to be seen faint rings and bands of the salt.

I desire to record my indebtedness to Dr. J. W. Nicholson for proposing to me the problem.

31 Linton Road,
Oxford.
11th February, 1925.

CXXIV. *The Crystal Structure of Lithium Potassium Sulphate.* *By* A. J. BRADLEY, *M.Sc., Ph.D., The Physical Laboratories, University of Manchester* *.

1. *The Marshalling of the Structure.*

LITHIUM potassium sulphate and the isomorphous lithium rubidium sulphate are the only two simple hexagonal sulphates known, and it therefore seemed possible that an investigation of their structure might be comparatively easy and would yield valuable information. $LiKSO_4$ has an axial ratio $c:a=1\cdot6755:1$ and a density 2·393 †. Its symmetry is hexagonal polar C_6, and is very well established by the general physical properties of the crystal and, in particular, by etch figures.

The method of investigation was originally the powder photograph, only very small crystals being then available. The apparatus and experimental methods have been described previously ‡. The spacings calculated from mean measurements of two films (Table I., Col. I.) fit on Hull and Davey's graph for a simple hexagonal lattice of axial ratio 1·675: 1, in good agreement with the crystallographic data. From these measurements, the volume of the unit cell which is a rhombic prism is $195\cdot5\times10^{-24}$ c.c. From the crystallographic data, the volume containing one molecule $LiKSO_4$ is $98\cdot0\times10^{-24}$ c.c., so that there are two molecules to the unit cell. The theoretical spacings for a structure consisting of a simple hexagonal lattice with two molecules to the unit cell are given in Col. II.

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* Communicated by Prof. W. L. Bragg, M.A., F.R.S.

† Groth, *Chemische Krystallographie*, ii. p. 329.

‡ Phil. Mag. xlvii. p. 657 (1924).

TABLE I.

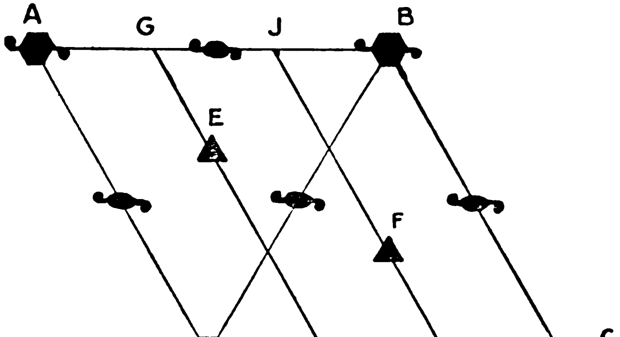
I. $\frac{d}{n}$ (obs.).	II. $\frac{d}{n}$ (calc.).	III. *hkil.*	IV. Intensity (calc.).	V. Intensity (obs.).
...	8·60	0001	...	...
...	4·445	$10\bar{1}0$	5	...
...	4·300	0002	26	...
3·94	3·950	$10\bar{1}1$	217	v.s.
3·09	3·090	$10\bar{1}2$	216	v.s.
...	2·867	0003	...	...
2·566	2·565	$11\bar{2}0$	120	v.s.
2·423	2·458	$11\bar{2}1$	73	w.
	2·408	$10\bar{1}3$	15	
2·186	2·220	$20\bar{2}0$	17	v.s.
	2·204	$11\bar{2}2$	158	
	2·150	0004	70	
	2·148	$20\bar{2}1$	16	
1·970	1·973	$20\bar{2}2$	56	f.s.
	1·936	$10\bar{1}4$	31	
1·912	1·912	$11\bar{2}3$	29	
...	1·754	$20\bar{2}3$	1	...
...	1·720	0005	...	...
...	1·679	$21\bar{3}0$	11	...
1·642	1·649	$11\bar{2}4$	52	s.
	1·648	$21\bar{3}1$	28	
1·595	1·604	$10\bar{1}5$	21	v.w.
1·560	1·563	$21\bar{3}2$	130	s.
...	1·544	$20\bar{2}4$	35	...
1·481	1·481	$30\bar{3}0$	89	s.
...	1·460	$30\bar{3}1$	0	...
...	1·450	$21\bar{3}3$	3	...
...	1·433	0006	3	...
...	1·429	$11\bar{2}5$	9	...
..	1·401	$30\bar{3}2$	9	...
1·367	1·364	$10\bar{1}6$	29	w.
	1·361	$20\bar{2}5$	13	
1·324	1·323	$21\bar{3}4$	30	v.w.
...	1·315	$30\bar{3}3$	0	...
1·286	1·282	$22\bar{4}0$	32	v.w.
...	1·268	$22\bar{4}1$	1	...
1·253	1·251	$11\bar{2}6$	66	m.
...	1·232	$31\bar{4}0$	9	...
...	1·229	0007	...	...
...	1·229	$22\bar{4}2$	22	...
1·223	1·220	$30\bar{3}4$	59	f.s.
	1·220	$31\bar{4}1$	18	
1·201	1·203	$20\bar{2}6$	17	v.w.
	1·201	$21\bar{3}5$	17	
1·187	1·185	$10\bar{1}7$	4	m.
	1·183	$31\bar{4}2$	70	

v.s. = very strong; s. = strong; f.s. = fairly strong; m. = medium; w. = weak; v.w. = very weak.

The powder photograph shows that there is no reflexion corresponding to (0001), (0003), or (0005), and this was confirmed by measurements made later on a single crystal by the spectrometer. A definite reflexion from (0002) can be observed by the spectrometer, though nothing is visible on the photograph.

The only space-group of symmetry C_6 for which the spacing (0001) is halved is C_6^6. There are also two other space-groups of higher symmetry which fulfil the same condition, namely C_{6h}^2 and D_6^6. These possess all the symmetry elements of C_6^6 in addition to certain extra elements, and therefore any space-group to which $LiKSO_4$ belongs must possess at least all the symmetry elements of C_6^6, which are shown in fig. 1.

Fig. 1.



⬢ represents a hexagonal screw axis of translation $\frac{c}{2}$, ▲ a threefold rotatory axis, and ● a twofold screw axis. These are the only elements of symmetry of C_6. A B C D represents a projection of the unit cell perpendicular to the hexagonal axes. Within this cell we have to place six ions, namely two each of K, Li, and SO_4. In order to preserve the symmetry these ions must go at the four corners A, B, C, D or at E and F, the centres of triangles ABD, DBC respectively. If any ion is placed at A, the other ion of the same type will also be placed at A. If any ion is placed at E, the corresponding ion will be placed at F, and *vice versâ*.

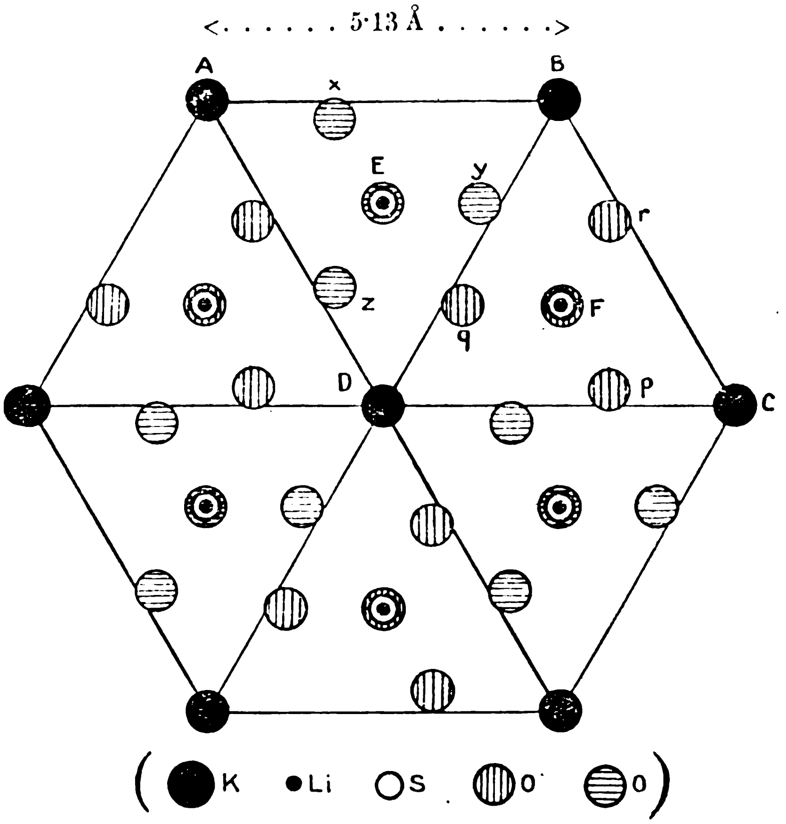
The arrangement of the oxygen atoms in the sulphate ion is determined by the symmetry of the crystal. Three of these atoms must be equidistant from the sulphur atom, and must lie in a plane perpendicular to the hexagonal axes of the structure. The fourth will lie so that the same hexagonal or trigonal axis passes through both it and the sulphur atom. Its distance from the sulphur atom will probably be different from that of the other three oxygen atoms, as its environment will be quite different; but, as will be shown later, the difference is too small to measure.

There are two possible positions for these sulphate ions: they may both be placed at A, or one may be placed at E and one at F. Intensity considerations alone can decide between these two structures. An examination of the powder photograph shows that the $(10\bar{1}0)$ plane gives no visible first-order reflexion, but a large third order. This must mean that the reflecting atoms are concentrated on planes AD, GH, JK, so that the reflecting power of each plane is almost the same; and hence if the sulphate ions are at A, the potassium ions are at E and F, and *vice versâ*. The strongest line on the film is due to the plane $(10\bar{1}2)$. It is therefore necessary to find a structure which gives only a minute $(10\bar{1}0)$ reflexion and a strong $(10\bar{1}2)$ reflexion.

It can easily be shown that any arrangement in which the sulphate ions are situated at A is impossible. They would completely outweigh the K and Li atoms at E and F, unless their oxygen atoms were so far from the sulphur atoms that the former reinforced the planes GH and JK, and were quite out of phase with the plane AD. On the other hand, if the sulphate groups are at A, a strong $(10\bar{1}2)$ reflexion will only be obtained if the oxygen atoms are crowded close to the centre of the sulphate ion. This is impossible, and therefore the sulphate ions are placed at E and F. In order to compensate these ions, it is necessary to put heavy atoms in the plane AD. The potassium atoms are therefore situated at A. The position of the lithium atoms cannot be fixed by X-rays, as they have an almost negligible effect on the intensity of the spectra; considerations of space and the distribution of positively- and negatively-charged ions indicate that they are situated at E and F.

The structure is shown in fig. 2, which is a projection perpendicular to the hexagonal axis. Potassium atoms are situated at A, and sulphur, lithium, and one oxygen atom at each of E and F. The remaining six oxygen atoms are at x, y, z, p, q, r. So far there are two parameters—the distance Ex and the angle FEy. The orientation of the second sulphate ion F pqr is then fixed by symmetry. The angle EFq is equal to the angle FEy, and FP is equal to Ex. This structure possesses no planes of symmetry parallel to the hexagonal axis unless FEy=0° or 60°.

Fig. 2.



2. *The Evaluation of the Parameters.*

A. Two parameters at right angles to the hexagonal axis.

The two parameters which fix the angle FEy (fig. 2) and the distance Ex can be found approximately by a study of planes parallel to the hexagonal axis. The angle ϕ (FEy) may vary between 0° and 120°, but values 60° and 120° are indistinguishable by X-rays from those between 60° and 0°. As the structure of a sulphate had never been completely elucidated, there was no estimate obtainable of size of the SO_4 group ; but it may be possible to get some idea of what is a likely value for E*x* by a consideration of the CO_3 group, which is one of the few complex acid radicles which have been fully investigated hitherto. In calcite the distance carbon to oxygen is 1·3 Å. The mutual repulsion of the oxygen atoms is overcome by the big charge on the carbon atom. It is probable that the oxygen atoms are drawn practically as close together as they can ever be. In the present instance they will tend to be pulled in further by the greater charge on the sulphur atom, but the greater size of the sulphur ion and the increased repulsion due to the extra oxygen atom will act in a reverse manner. It is therefore reasonable to suppose that the distance E*x* lies between 1·2 Å and 1·7 Å.

For the purpose of evaluating these parameters, reflexions were obtained from the face ($10\bar{1}0$) of a single crystal, using the X-ray spectrometer, with molybdenum radiation. The values obtained for the various orders of reflexion are given in Table II., Col. II.

Table II.

I. *hkl.*	II. Observed intensities. I.	III. Structure factor. A.	IV. $\frac{I}{A^2}$	V. Scattering power of oxygen.
0001	...	...	...	...
$10\bar{1}0$	9·5	2·1	2·15	10·0
0002	65·5	8·3	0·95	10·0
0003	...	...	...	...
$11\bar{2}0$	87·4	17·4	·29	7·3
$11\bar{2}1$	27·5	10·0	·275	7·0
$20\bar{2}0$	18·5	7·5	·33	6·5
0004	167·0	27·5	·22	6·3
$11\bar{2}3$	7·4	8·2	·11	5·7
0005	...	...	...	...
$30\bar{3}0$	62·5	26·0	·092	4·3
0006	8·8	9·2	·10	4·0
$11\bar{2}5$	3·9	5·9	·11	4·0
$40\bar{4}0$	1·8	5·3	·064	2·0
$11\bar{2}7$	0·3	2·8	·04	2·0
$50\bar{5}0$	0·45	7·6	·008	...
$60\bar{6}0$	3·5	19·0	·010	...
$90\bar{9}0$	0·5	19·0	·001	...

The relative values of the observed intensities for ($10\bar{1}0$) and ($30\bar{3}0$) confirm the deductions made from the powder photograph for the marshalling of atoms in planes parallel to ($10\bar{1}0$). Structure factors for the various orders of reflexion from $(10\bar{1}0)$ were calculated for various values of ϕ between 0° and 60°, and of Ex between 1·2 and 1·7. Whatever reasonable assumptions be made as to the relative scattering powers of the different atoms, calculation shows that for almost any values of the parameters within the above limits the reflexion from $(10\bar{1}0)$ will be weak, but that from $(30\bar{3}0)$ will be strong. From the observations made by the spectrometer it is clear that the structure factor of $(20\bar{2}0)$, which alters rapidly with a change in ϕ, must be of an intermediate size. This can only be the case if ϕ has a value round about 30°, say between 25° and 35°, and its precise value can be fixed very accurately if we know the exact value of Ex. A comparison of the intensities $(10\bar{1}0)$, $(20\bar{2}0)$, and $(30\bar{3}0)$ with that of $(11\bar{2}0)$ shows that the plane $(11\bar{2}0)$ must have a structure factor intermediate between that of $(20\bar{2}0)$ and $(30\bar{3}0)$. This is actually the case if ϕ is about 30°, unless Ex is very small. Any value greater than about 1·3 Å is admissible. If $Ex = 1{\cdot}4$ Å, ϕ must be almost exactly 30°; and this seems to be the most reasonable value to choose for Ex, for any appreciably larger value brings oxygen atoms of neighbouring SO_4 groups too close together.

The positions of the oxygen atoms in fig. 2 have now been determined. From a consideration of the reflexions from planes parallel to the hexagonal axis, the angle FEy is about 30°, and the distance Ex is not less than 1·3 Å. Spatial considerations indicate that it is not greater than about 1·5 Å.

B. Parameters parallel to the hexagonal axis.

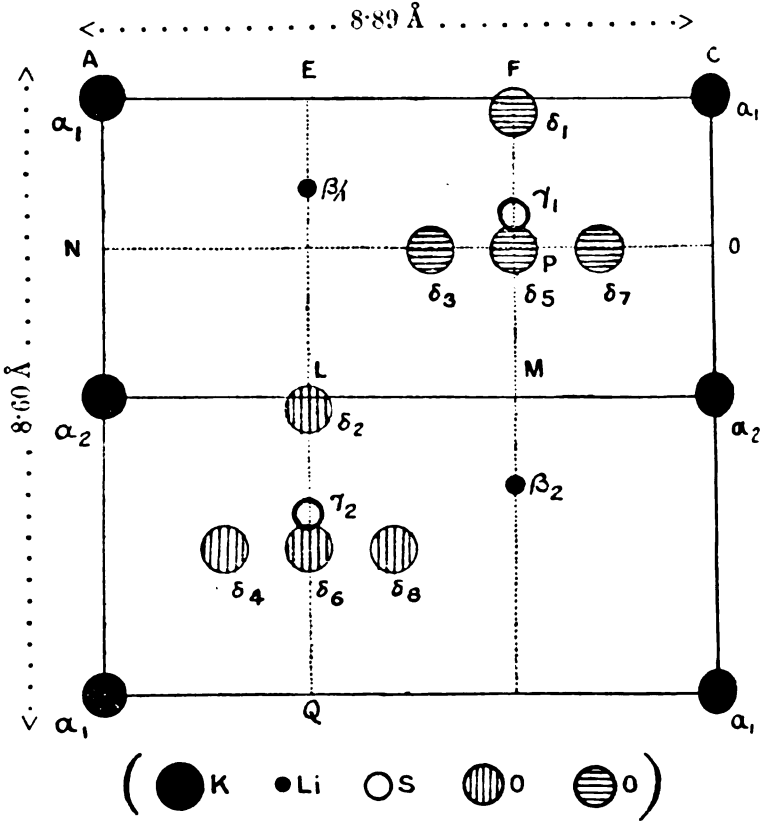
The distribution of atoms along the hexagonal axis can be partially determined by a study of the spectra from planes (0001). All odd orders of reflexion are absent; the ions are therefore arranged in pairs along the hexagonal axis, so that the (0001) spacing is halved. The atoms are arranged in the manner shown in fig. 3. This is a projection of the unit cell through AC parallel to the hexagonal axis. α, β, γ, δ are potassium, lithium, sulphur, and oxygen atoms respectively.

If we regard the positions of the potassium atoms as fixed, the positions of the lithium and sulphur atoms are determined by the parameters $E\beta_1 = M\beta_2$ and $F\gamma_1 = L\gamma_2$ respectively. In order to fix the positions of all the oxygen atoms four independent parameters must be determined. Two of these have already been fixed. The two remaining parameters are $\gamma_1\delta_1 = \gamma_2\delta_2$, which fixes the position of the oxygen atom at δ_1, and the distance $\gamma_1 P$ of γ_1 from the line

δ_3 δ_5 δ_7, which fixes the position of the other three oxygen atoms.

Of the even orders from (0001), which alone occur, the only strong reflexions are (0002) and (0004), and the second of these is nearly three times as strong as the first. The phase factor for (0004) like that for $(30\bar{3}0)$ is therefore very nearly normal. (0006) is quite small. This shows that the atoms are concentrated in planes AC and LM, and also in planes half-way between, NO (fig. 3). The comparatively small reflexion from (0002) requires planes AC and NO to be almost equal in reflecting power. This will be the case if γ_1, δ_3, δ_5, δ_7 are situated close to NO, and δ_1 as well as α_1 is on or near AC. Very little variation in these positions is allowable.

Fig. 3.



It is reasonable to suppose that the sulphur atom is approximately at the centre of the tetrahedron formed by the surrounding oxygen atoms. In this case $\gamma_1 P = \frac{1}{3}\gamma_1 \delta_1$. Since δ_1 is almost in the plane AC, and P is almost in the plane NO, γ_1 P is approximately one-quarter AN, *i. e.* 0·5 Å. The distance of the odd oxygen atom of the SO_4 group from the central S atom ($\delta_1 \gamma_1$) must be about 1·5–1·6 Å; for if it were more, this oxygen atom would approach too close to the nearest oxygen atoms of the next SO_4 groups (*e. g.* δ_2 would be too near δ_3), and if it were less, δ_1 would be too far from the plane AC. This value is exactly the same as the distance of the other oxygen atoms calculated from $Ex = 1{\cdot}4$ and $\gamma_1 P = 0{\cdot}5$; so that, as nearly as one can estimate, the four oxygens of the SO_4 group are situated at the corners of a regular tetrahedron. The position of the lithium atom is somewhat uncertain. β_1 may be anywhere along the line EL. In any case it is likely to be fairly close to the three oxygen atoms such as δ_3, but it may be either above or below δ_3. As there is quite a big space in the structure above δ_3 and very little room below, it very likely goes above.

The approximate position of all the atoms in the structure has thus been determined independently of any assumption with regard to the relative extent to which the atoms of different elements scatter radiation at different angles of reflexion. In order to obtain any more precise definition of the parameters and to check the agreement between observed intensities of reflexion and calculated values, it is necessary to make some assumptions. Some information can actually be obtained as to the relative scattering power of oxygen. Planes $(11\bar{2}1)$, $(11\bar{2}3)$, $(11\bar{2}5)$, $(11\bar{2}7)$ have exactly the same phase factor; the Li, K, and S atoms are spaced in pairs in such a way that each atom is exactly out of phase with the other of the same kind. We are therefore dealing with oxygen atoms only, and these are arranged in precisely the same way in each of the four planes.

Reflexions from these planes were obtained by means of the spectrometer (see Table II.). The intensity of reflexion diminishes very rapidly with increasing glancing angle, which shows that the oxygen atoms are very inefficient reflectors at large glancing angles. As a rough approximation, the relative scattering powers of K and S have been assumed to be proportional to the number of electrons in each atom when fully ionized; thus K = 18, S = 10. This is probably not far from the truth over most of the range of angles considered here. Perhaps the value of S is rather low, particularly for large angles. On the other hand, it is clear that the scattering power of oxygen falls off so much more rapidly that it cannot be represented by a constant in the same way. A comparison of the reflexions (11$\bar{2}$1), (11$\bar{2}$3), (11$\bar{2}$5), (11$\bar{2}$7) with that of (30$\bar{3}$3) has led to the figures for the scattering power of O relative to S and K, which are given in Table II., Col. V., though of course these are only to be regarded as approximate. These figures have been used to calculate structure factors for all the other planes.

Some allowance has been made for the lithium atoms, but in any case the effect of the lithium atoms is so small as to make no appreciable difference. The uncertainty as to the relative scattering powers of the other three kinds of atom is much more serious, and will certainly give rise to quite large errors.

In consequence, too much reliance cannot be placed on individual agreement or divergences between observed and calculated intensities. Moreover, there is as yet no knowledge of the part played by "extinction"[*] in reducing the intensity of the stronger reflexions. One can therefore only hope for a rough general agreement between the observed and calculated intensities. The comparison is made the most easily by arranging the planes in descending order of magnitude of spacing. The intensity of reflexion I should be proportional to the product of the square of the structure factor A and a factor which falls off steadily as the glancing angle increases. The quotient $\frac{I}{A^2}$ should therefore show a gradual decrease as we pass from planes with large spacings to those with small spacings. Column IV. shows that this is the case.

This method of comparison was first used by W. L. Bragg[†] for the case of aragonite, except that he found that the intensity was more nearly proportional to the structure factor itself. This is certainly not the case in the present instance[‡].

The precise value of the parameter $\gamma_1 F$ used for calculating the values of A shown in the table was obtained in the following way. The spectrum from (0006) was quite small, whilst that from (11$\bar{2}$6) as observed on the powder photograph was quite appreciable. This is only the case if $\gamma_1 F$ lies about 1·7 Å. The other values employed were $\phi = 30^\circ$, $Ex = 1{\cdot}4$ Å, $\gamma_1 P = 0{\cdot}5$ Å, $\gamma_1\delta_1 = 1{\cdot}5$ Å, $L\beta_1 = 3{\cdot}0$ Å.

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[*] W. L. Bragg, R. W. James, and C. H. Bosanquet, Phil. Mag. xlii. p. 1 (1921); C. G. Darwin, Phil. Mag. xliii. p. 800 (1922).

[†] W. L. Bragg, Proc. Roy. Soc. A, cv. p. 16 (1924).

[‡] Compare G. Greenwood, Phil. Mag. xlviii. p. 654 (1924).

In order to check by the powder photograph the values allotted to the various parameters, a complete determination was made of the calculated intensities of all the planes down to $(31\bar{4}2)$. The structure factors were calculated in the usual manner; and in each case the square of the structure factor was multiplied by a factor N, which is the number of co-operating sets of planes, and by the angular factors for the powder method. The latter was assumed to be proportional to the square of the cosecant, as in the case of arsenic*. The values calculated by this means are shown in Table I., Col. IV. They may be compared with the observed intensities for the powder photograph shown in Table I., Col. V.

On the whole the agreement is reasonably good, and provides a satisfactory confirmation of the values allotted to the various parameters, which were fixed by the spectrometer method. The factor allowing for the change of the relative scattering power of oxygen was assumed to have the values calculated very approximately from the spectrometer measurements. A large error may be introduced in the calculations of certain reflexions on this assumption. The plane $(11\bar{2}1)$ in particular seems to show this effect.

The Results of X-Ray Analysis.

The structure of $LiKSO_4$ is shown in projection in figs. 2 and 3. The unit cell is a hexagonal prism of base AB = 5·13 Å and height EQ = 8·60 Å. The potassium ions are situated on a simple hexagonal lattice of axial ratio $a : c = 1 : 0{\cdot}838$. The sulphate ions comprise two simple hexagonal lattices of axial ratio $a : c = 1 : 1{\cdot}6755$, which fit together as if the sulphate ions were spheres in hexagonal close-packing. Lithium ions alternate with sulphate ions. Each sulphate ion has six potassium ions as neighbours, and each potassium ion is surrounded by six sulphate ions.

The oxygen atoms are arranged around the sulphur atom of the sulphate group in tetrahedral fashion. Three oxygen atoms must be equidistant from the central sulphur atom, and the distance of the fourth cannot be much different. The actual distance is found to be 1·5–1·6 Å. A model of the structure was made on a scale of 1 Å to 1 cm., the atoms being represented as spheres with the following radii:—K = 1·34, Li = 0·79, O = 1·36. These values were suggested by Prof. Bragg, the values originally proposed by him* being modified in the manner suggested by Wasastjerna †. The model shows oxygen atoms belonging to neighbouring sulphate groups in contact, but there is more space for the potassium and lithium atoms than is actually filled by them.

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* Phil. Mag. *loc. cit.*

A remarkable fact is the closeness between the axial ratio of $LiKSO_4$ (1·6755) and the theoretical value for a system of spheres in close-packing (1·633). In the case of the isomorphous $LiRbSO_4$, the value is still closer (1·6472). This suggests that the sulphate group, which is by far the largest entity in the crystal, is the chief factor in deciding the nature and dimensions of the crystal. Viewed in this light, the structure is formed by the closest hexagonal packing of sulphate ions, the latter being roughly spherical in shape.

The size of the unit is thus determined almost solely by the size of the sulphate ions, the metallic ions filling up as far as possible the interstices of the structure. The rubidium or potassium and lithium atoms appear to be nearly the right size for this purpose, the structure being scarcely distorted from the ideal axial ratio. The loose packing of the potassium atoms as shown by the model may arise from the possibility that the sulphate group is not best represented as four separate spheres of oxygen, but that there is, in addition, a sphere of influence due to the sulphate ion as a whole, so that metallic ions are driven away from the hollows between neighbouring oxygen atoms. Such a supposition would explain the remarkable value of the axial ratio, and would show that the metallic atoms are actually packed quite tightly into the structure.

It should be noted that the space-groups C_{6h}^2 and D_6^6 are ruled out by the absence of planes of symmetry in the structure, so that the space-group of the complete arrangement is C_6^6, in complete correspondence with the crystallographic evidence. The structure possesses enantiomorphism, owing to the asymmetrical arrangement of the oxygen atoms about the hexagonal axes. Thus the parameter ϕ (FEy, fig. 2) may be either 30° or 90°, the difference between these two arrangements being due to the lack of an equatorial plane of symmetry; but there is no possibility of distinguishing between the two enantiomorphous arrangements by means of X-rays. Wulff and others have, however, found that there are two distinct types of crystal, one of which is lævo- and the other dextro-rotary, and this would appear to show that crystals exist with either of the two possible values of ϕ. Normally, as Wulff has shown, a lamellar twin is formed by layers of the two types alternating along the optic axis, so that no rotary polarization can be observed. This is precisely what might be expected from the structure. A new layer of SO_4 groups which is deposited on a (0001) face may either fall into the same position as the layer next but one previously, and so make a normal repetition of the structure, or it may commence an enantiomorphous crystal without the slightest distortion of the lattice. In this case a layer of K atoms (*e. g.* $\alpha_2\,\alpha_2$ in fig. 3) is common to both twins. In fig. 2 we shall have $E\hat{F}q = 120^\circ - F\hat{E}y = 90^\circ$, but fig. 3 will be unaltered.

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* W. L. Bragg, Phil. Mag. xli. p. 169 (1920).

† J. A. Wasastjerna, "On the Radii of Ions," Soc. Scient. Fenn., Comm. Phys.-Math. i. p. 38 (1923).

Summary.

The crystal structure of $LiKSO_4$ consists of a system of sulphate ions in hexagonal close-packing, alternating with metallic ions. The potassium ions form a simple hexagonal lattice, while the lithium ions are arranged like the sulphate groups.

The lattice dimensions were fixed from a powder photograph, the unit cell being a prism of base 5·13 Å and height 8·60 Å and containing two molecules of $LiKSO_4$. The space-group is C_6^6.

The parameters fixing the relative positions of the different kinds of atoms were evaluated from intensity measurements made by the X-ray spectrometer. The position of all except the lithium atoms was fixed by this means, the position of the latter being determined by spatial considerations. The sulphate ion is a tetrahedron of oxygen atoms surrounding a central sulphur atom, the distance S–O being 1·5–1·6 Å.

I take this opportunity of expressing my thanks to Messrs. R. W. James, M.A., and G. Greenwood, M.Sc., to whom I am indebted for the spectrometer measurements. I desire to thank Prof. W. L. Bragg, F.R.S., and Mr. James for the great interest they have taken in this work and for their advice and guidance. Part of the apparatus used was purchased from money kindly given to the Physical Laboratory by the Government Grant Committee of the Royal Society and by Messrs. Brunner, Mond. During all except the concluding stages of the work the Author was in receipt of a grant from the Board of Scientific and Industrial Research. I wish to thank Messrs. Metropolitan-Vickers for the opportunity of concluding this work.

CXXV. *The Behaviour of Hydrogen in the Discharge due to Alternating Electric Fields of High Frequency.* *By* R. Winstanley Lunt, *M.Sc.*, *Ph.D.*, 1851 *Exhibition Senior Student* *.

Introduction.

ARISING out of a research about to be published elsewhere (Proc. Roy. Soc. May 1925) on the chemical effects in gases produced by coronas due to alternating electric fields of frequency of the order of 10^7 cycles per second, is the question of the incidence of the ionization produced by such fields on the chemical changes which have been observed.

An attempt has now been made to carry out a preliminary investigation of the ionization produced in hydrogen at the frequency $1{\cdot}5 \times 10^7$.

An analysis of the current voltage relationships occurring in an ozonizer or ionization vessel is put forward, in the light of which, as far as possible, all results will be discussed. Its chief claim to consideration lies in its simplicity compared with that of the only analysis of consequence extant, namely that of Warburg †.

A complete description of the apparatus and of the experimental technique is to be found in the communication to which reference has been made already.

The Current Voltage Relationships occurring in an Ozonizer or Ionization Vessel.

The problem is conveniently restricted to the standardized type of vessel consisting essentially of two concentric glass or quartz tubes, the outer surface of the outer tube and the inner surface of the inner tube being arranged to serve as electrodes.

This arrangement constitutes a system of three condensers in series: the capacity C_1 of the outer wall, the capacity C_2 between the inner surface of the outer tube and the outer surface of the inner tube, and the capacity C_3 of the inner wall. It may therefore be represented in the conventional symbols as in fig. *a*, where it is assumed that for all practical purposes the power factors of C_1 and C_3 are negligibly small.

When the gas in the ozonizer is ionized, it is seen that this is equivalent, for any given value of the ionization, to a resistance R shunting the condenser C_2. The system now becomes as in fig. *b*, which is itself electrically equivalent to fig. *c*, where $\frac{1}{C_4}=\frac{1}{C_1}+\frac{1}{C_3}$.

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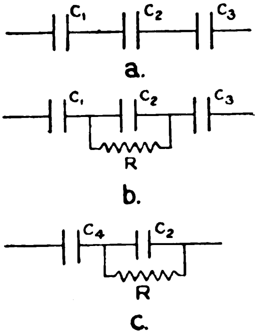
* Communicated by Professor F. G. Donnan, F.R.S.

† Warburg, *Ann. d. Phys.* xxviii. pp. 1-17 (1909).

Figs. *a*, *b*, *c*.



a.

b.

c.

Now let V be the total voltage applied to the system, and I the total current, and let these be out of phase by an angle ϕ.

Let $f=\frac{\omega}{2\pi}$ be the frequency, and let V_4 be the voltage across the condenser C_4.

Then

$$I=j\omega C_4V_4, \quad \ldots\ldots\ldots \quad (1)$$

where $j=\sqrt{-1}$.

Let I_2 be the current through C_2,
and I_R be the current through R,
and V be the voltage across R and C_2.

Then

$$I_2=j\omega C_2V_2. \quad \ldots\ldots\ldots \quad (2)$$

Let W be the power consumed in the system in watts.

Then

$$W=VI\cos\phi.$$

Consider the vector diagram of V and I (fig. *d*).

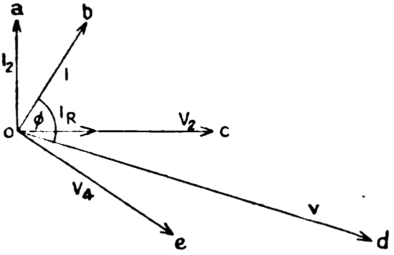
There is an associated voltage V_4 given by equation (1) in quadrature with I. Subtraction of vectors gives the voltage V_2 across the ionization space. The current in phase with V_2 and responsible for the energy generated in the system is given by

$$I_R=\frac{W}{V_2}.$$

And by subtraction of vectors the displacement current I_2 across the ionization space is obtained.

Thus having determined experimentally V, I, and W, and knowing C_1, C_2, and C_3 by direct measurement, it is possible to evaluate V_2 and I_R. Further, since W is constant for any given value of I, it seems reasonable to consider that the corresponding intensity of the ionization is of a constant mean value, which is attained when the rate of formation of new ions by collisions is equal to the rate of de-ionization. It follows then that R has a constant mean value, and that I_R may be identified with the current carried by the ions.

Fig. *d.*



d.

This procedure is open to two objections. Firstly, that surface charges may arise on the quartz walls which will result in the potential gradient in the ionization space being different from that due to V_2 alone, and consequently the value of I_R as given by

$$I_R = \frac{W}{V_2}$$

would be in error. While it is somewhat difficult to see in what way such charges could arise in an alternating field, experiments are being devised to investigate the point, and will form the subject of another communication.

Secondly, it may be contended that the current carried by the ions may be zero except during the short intervals of time during which the potential is near its maximum value. This is equivalent to the contention that the ionization is not continuous. It has been found that the potential across the whole system V necessary to produce ionization by collision for any given gas-pressure is from three to six times greater than the maximum value of V applied when ionization has been established. And that when the ionization, as evidenced by visual corona, has been destroyed by a momentary diminution in V, it is never possible to re-establish the ionization unless V be increased to the value initially requisite to produce ionization. It may be concluded, therefore, that the ionization and the current carried by the ions are continuous.

When the values of V are too low to be read directly, it is possible to proceed to an approximate evaluation of V_2 and I_R in the following way.

Consider the vector diagram when $\frac{I_R}{I_2} \leqq 0\cdot2$; that is, when $a\hat{o}b$ lies between $0^\circ\cdot0$ and $11^\circ\cdot2$.

Since $a\hat{o}b = c\hat{o}e$, we have the approximate relation

$$\begin{aligned} V &= V_2 \cos \tfrac{1}{2}(a\hat{o}b) + V_4 \cos \tfrac{1}{2}(a\hat{o}b) \\ &= 0\cdot995 V_2 + 0\cdot995 V_4 \,; \end{aligned}$$

that is, within the experimental error in determining V,

$$V = V_2 + V_4.$$

A first approximation to V_2 is given by

$$V_2 = \frac{I}{j\omega C_2},$$

and to I_R by

$$I_R = \frac{W}{V_2},$$

and to I_2 by

$$I_2 = \bar{I} - \bar{I}_R.$$

A second approximation to V_2 is given by

$$V_2'' = \frac{I_2}{j\omega C_2},$$

and to I_R by

$$I_R'' = \frac{W}{V_2''}.$$

From the values obtained for I_R, an approximate determination of the intensity of ionization can be obtained by an extension of the analysis obtaining for liquid electrolytes, which is expressed in the following way:

$$i = (U_0 + V_0) A N X e, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where i is the total current carried by the ions, A the cross-sectional area through which it flows, N the number of pairs of ions per c.c. (in an enclosed mass of gas the number of negative and of positive ions must be identical), e the electronic charge, X the voltage gradient, and (U_0+V_0) the sum of the mobilities of the ions. As a first approximation it may be assumed that the positive ions bear a single charge, which is known to be very nearly true since the fraction of ions bearing a higher charge is extremely small*. The experimental values obtaining for the quantity X/p indicate that the negative ions are electrons †.

If U_H represents the mobility of the positive ion in hydrogen at 760 mm. and 15° C., W the velocity of the negative ion, and p the hydrogen pressure in mms. Hg, the above equation becomes

$$i=\left(\frac{760XU_H}{p}+W\right)ANe, \quad . \quad . \quad . \quad . \quad (4)$$

since it is known that the velocity of the positive ions in hydrogen varies directly as X/p; the value chosen for the calculations in this communication is that of Lattey and Tizard ‡. W is known as a function of X/p within the range of values of this quantity obtaining in the experiments now to be described §, and the mean value has been calculated by assuming the applied voltage to be sinusoidal. The values of $i=I_R$ and of X (r.m.s.) being known from the preceding analysis, it becomes a matter of simple arithmetic to evaluate to a first approximation the mean value N of the equilibrium ionization.

EXPERIMENTAL.

Preparation of Gas.

Hydrogen, obtained from a cylinder, was scrubbed through concentrated sulphuric acid and dried by passing over 3 feet of phosphoric anhydride. It was found to contain about 0·2 per cent. of oxygen.

Ionization.

Five series of experiments were carried out with the gas at 12·5, 19·5, 26, 35, and 47 cm. at 20° C. respectively, and in each the frequency $1·5\times10^7$ was applied.

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* J. S. Townsend, 'Electricity in Gases,' Oxford, 1915.

† Lattey & Tizard, Proc. Roy. Soc. A. lxxxvi. p. 349 (1912).

‡ Lattey & Tizard, *loc. cit.*

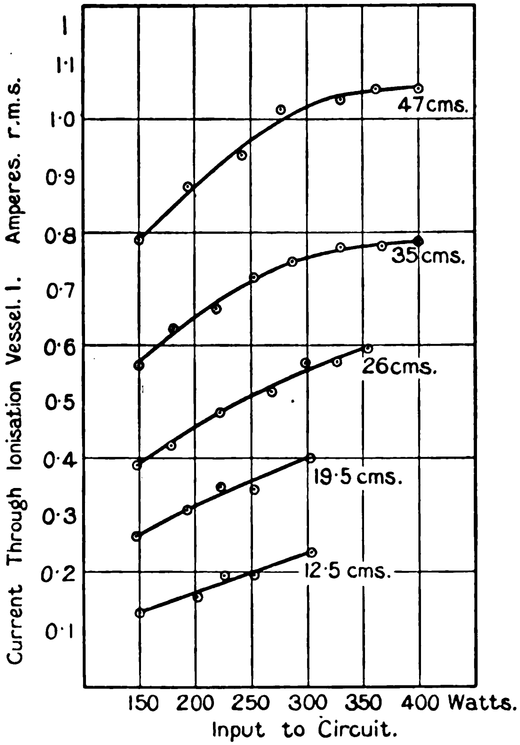
§ Lattey & Tizard, *loc. cit.* Townsend & Bailey, Phil. Mag. (6) xlii. p. 873 (1921).

At each of these pressures and for input wattages to the oscillating circuit over the range 150–400 the following quantities were determined :—

(1) The rate of generation of heat in watts, W, in the reaction vessel.
(2) The current, I, flowing through the ionization vessel.
(3) The voltage, V, maintaining this current through the vessel.

The values obtained are given in figs. 1, 2, and 3 respectively.

Fig. 1.—Current flowing through Ionization Circuit.



In order to obtain strictly comparative readings, it was found essential to maintain the filament current of the valve at a constant value, which was fixed at 6·5 amperes.

Fig. 2.—Heat generated in Ionization Vessel.

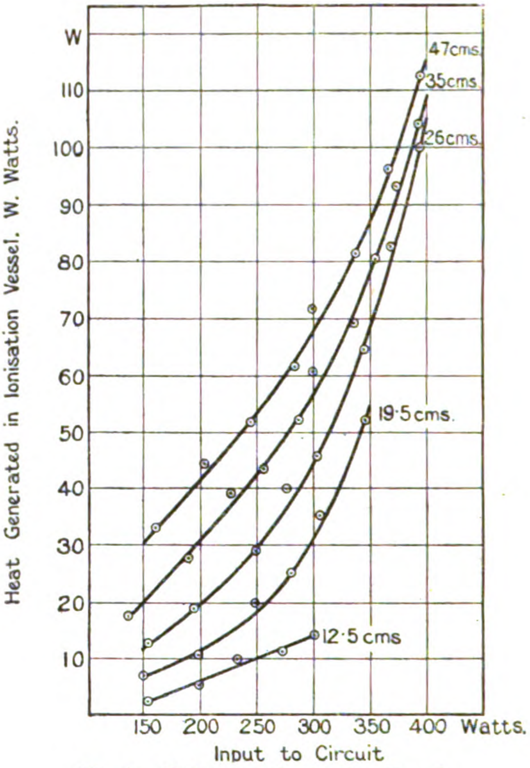
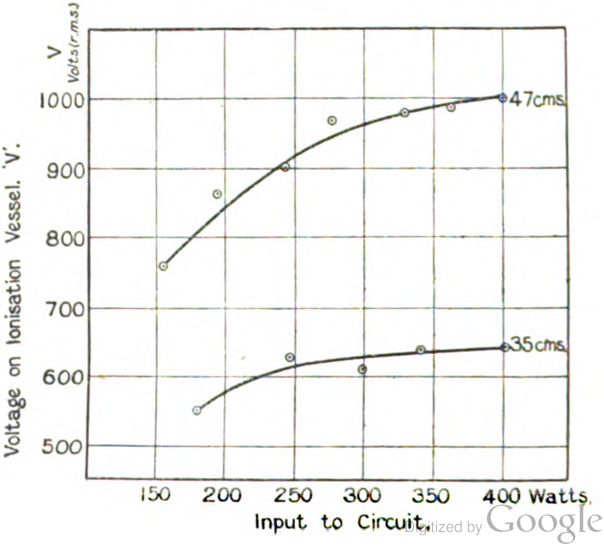


Fig. 3.—Voltage on Ionization Vessel



Owing to the low value of the voltage across the ionization vessel over the lower end of the pressure range, this was determined for the pressures 35 and 47 cm. only. Also due to the fact that over the lower portion of the pressure range the valve efficiency is low and the anode dissipation correspondingly high, it was impracticable to operate with input watts above about 300.

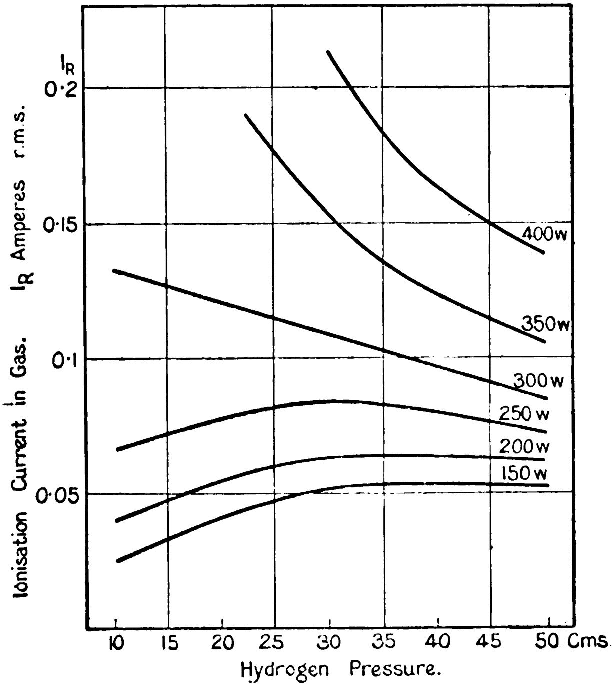
From the above values, in the manner already indicated, the corresponding values of the following quantities have been calculated :—

(1) The ionization current I_R (fig. 4).

(2) The ratio of the r.m.s. voltage gradient, X, in volts per cm. in the gas to the gas-pressure, *p*, expressed in mm. Hg at 15° C. (fig. 5).

(3) The ratio of the mean intensity of ionization, N, to the number of molecules per c.c., N_0, at the given pressure and at 15° C. (fig. 6).

Fig. 4.—Ionization Current.



For the sake of convenience and simplicity, the above-mentioned quantities have been expressed as functions of the hydrogen pressure over the range 10 to 50 cm. the input watts being treated as a parameter varying over the range 150 to 400 watts.

Fig. 5.—Voltage Gradient in the Ionized Hydrogen.

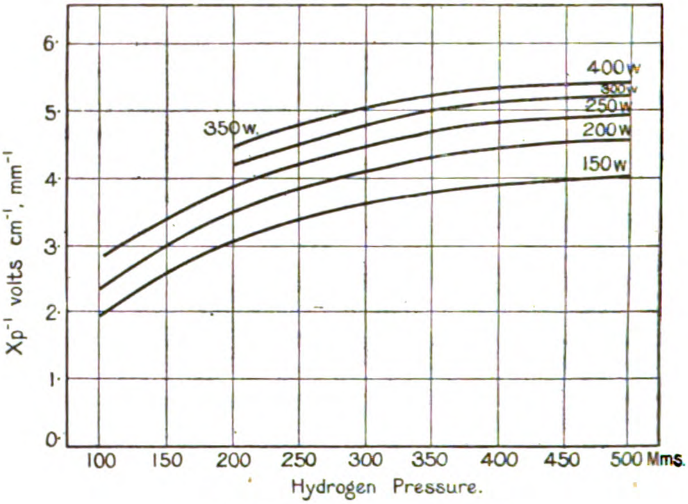
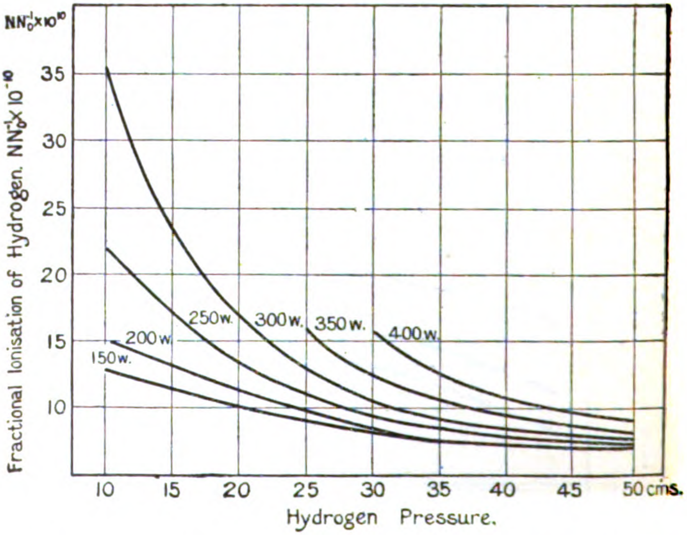


Fig. 6.—Mean Intensity of Ionization.



It is of some interest to consider the "equivalent temperature' of the ionized hydrogen—*i. e.*, that temperature at which the same density of ionization would be produced by thermal dissociation as that observed in the ionization vessel under any given conditions.

In the following attempt to estimate the equivalent temperature, which is advanced very tentatively, it is assumed that the amount of monatomic hydrogen in existence during the discharge is negligible, and not greater than 1 or 2 per cent. of the total hydrogen. This assumption appears to be warranted by experiment. No appreciable increase in pressure has been observed when the hydrogen is ionized, except that due to a slight increase in temperature.

Consider the equations:

$$\tfrac{1}{2}H_2 = H, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$K_1 = \frac{p_H}{p_{H_2}^{\frac{1}{2}}},$$

$$F_1 = 81000 - 3{\cdot}5T \log_e T + 0{\cdot}00045T^2 + 1{\cdot}17T\;{}^{*};$$

$$H = H^+ + e, \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$K_2 = \frac{p_{H^+} \times p_e}{p_H} = \frac{p_{H^+}^{\,2}}{p_H},$$

$$F_2 = \frac{23070}{RT} V_i - \frac{5}{2} \log_e T - \left(\frac{5}{2} - \frac{3}{2} \log_e M_e - \frac{S_1}{R}\right){}^{\dagger},$$

where p denotes the partial pressure of the material indicated by its suffix,

K_1 ,, the equilibrium constant of the reaction represented by equation (1),

F_1 ,, the decrease in free energy of the reaction represented by equation (1),

e ,, an electron,

H ,, a positive hydrogen ion,

K_2 ,, the equilibrium constant of the reaction represented by equation (2),

F_2 ,, the decrease in free energy of the reaction represented in equation (2),

T ,, the absolute temperature,

V_i ,, the ionization potential in volts (Hydrogen $= 13{\cdot}5$ volts),

M_e ,, the molecular weight of an electron;

and S_1 is given by

$$S_1 = -3{\cdot}2 \text{ cal. deg.}^{-1}\;{}^{\ddagger}.$$

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[*] Lewis & Randall, 'Thermodynamics' (New York, 1923).

[†] Foote & Mohler, 'Origin of Spectra' (New York, 1923).

[‡] Tollman, Journ. Amer. Chem. Soc. xlii. p. 1185 (1920); xliii. p. 1592 (1921).

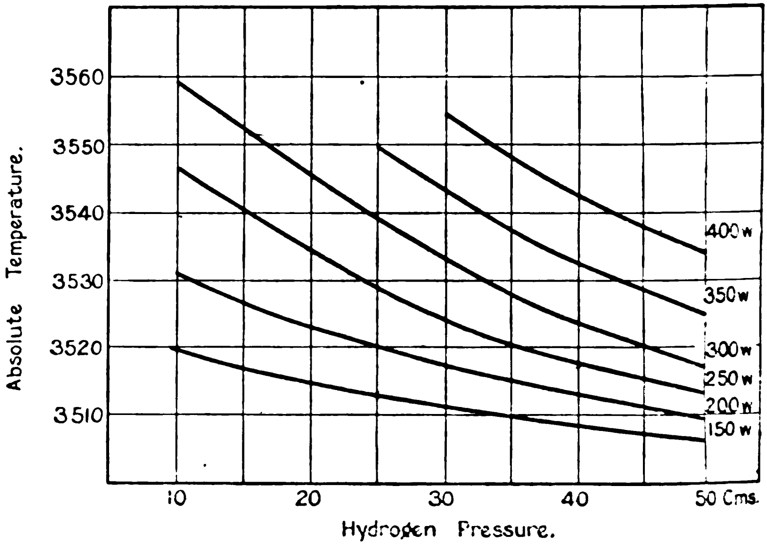
Then

$$K_1K_2 = \frac{p^2_{H^+}}{p^{\frac{1}{2}}_{H_2}} \quad \text{and} \quad p_{H^+} = \sqrt[4]{K_1^2K_2^2 p_{H_2}}$$

on the above assumptions.

K_1 and K_2 having been calculated from the foregoing free energy equations, the values of $\log \frac{p_{H^+}}{p_{H_2}}$ (equilibrium values) have been plotted against the absolute temperatures at which they are in equilibrium as abscissæ for the following values of the hydrogen pressure:—$p_{H_2} = 10, 20, 30, 40, 50$ cm.

Fig. 7.—Equivalent Temperature of Hydrogen



The quantity $\frac{p_{H^+}}{p_{H_2}}$, provided the partial pressure of monatomic hydrogen can be neglected, is identical with that represented by $\frac{N}{N_0}$. Knowing $\frac{N}{N_0}$ as a function of p_{H_2} for various input watts, the corresponding values of the "equivalent temperature" for $p_{H_2} = 10, 20, 30, 40, 50$ cm. Hg 15° C. can be read off. The resulting values are given graphically in fig. 7.

It must be observed, however, that the thermal reaction at the "equivalent temperature" would correspond to an almost complete dissociation into monatomic hydrogen.

SUMMARY.

(1) An analysis of the Siemen's Ozonizer is put forward which affords a ready determination of the voltage gradient and of the current carried by the ions in the gas.

(2) An attempt has been made to determine the approximate mean intensity of ionization in hydrogen under any given electrical conditions by a simple equation relating the conduction current in the ionized gas to the known motions of ions and electrons in hydrogen and to the impressed electric force.

(3) The two quantities, the impressed electric force and the resulting mean fractional intensity of ionization in hydrogen, have been determined at the frequency $1{\cdot}5 \times 10^7$ over the pressure range 10 to 50 cm. and over the available range of electrical conditions.

(4) The concept of "equivalent temperature" is discussed with reference to the discharge in hydrogen.

In conclusion, the author wishes to express his indebtedness and thanks to the Royal Commissioners for the Exhibition of 1851 for a Scholarship, and to the Trustees of the Ramsay Memorial Fellowship Trust for a Fellowship, which have enabled the above work to be carried out; to Messrs. The Marconi Wireless Telegraph Company, and to Mr. E. Green, M.Sc., of that Company; to Messrs. Brunner, Mond & Company, for the loan of apparatus; to his friend Mr. F. D. Smith, M.Sc., to whom he owes the vector solution of the Siemen's Ozonizer; to Professor C. L. Fortescue, of the City & Guilds' Engineering College, South Kensington; and especially to Professor F. G. Donnan, F.R.S., at whose suggestion the work was undertaken, for his deep interest and suggestive advice during the progress of the research.

The William Ramsay Inorganic and
Physical Chemistry Laboratories,
University College, London.

CXXVI. *A Note on Musical Atmospheric Disturbances.* *By* T. L. ECKERSLEY, *M.A., Research Department, Marconi's Wireless Telegraphy Co.**

IT has been known to workers in "Radio" for some years that if a telephone or any other audio-recorder system is placed directly in series with a large aerial, disturbances of a musical nature can be heard.

These have a very peculiar character: the pitch of the note invariably starts above audibility, often with a click, and then rapidly decreases, finally ending up with a low note of more or less constant frequency which may be of the order of 300 to 1000 a second.

The duration of the complete disturbances varies very considerably; at times it may be a very small fraction of a second, and at others it may be even 1/5 of a second.

Some workers have noticed a regular diurnal variation in the character and frequency of these disturbances. In the early morning disturbances of this type are very infrequent and the duration is short. The frequency and duration increase as the day advances, and may be very considerable towards the late afternoon and evening. They are greatest during the night.

These disturbances are obviously of an external origin, and do not owe their character to the resonance of the receiver system under "shock excitation." The explanation offered here is based on Dr. Eccles' theory of ionic refraction, and may be able to yield data of considerable importance relating to the physical constants of the "upper conducting layer," which plays such an important part in radio transmission.

Briefly, the occurrence of these disturbances is attributed to the dispersion of an electrical impulse in a medium loaded with ions.

For, as Dr. Eccles has shown, the presence of free ions has the effect of apparently decreasing the specific inductive capacity of the medium by an amount depending on the frequency of the waves travelling through it.

The loading effected by the free ions gives the medium a dispersive character, since the transmission constants vary with the frequency of the impressed waves. Under these conditions we have, as is well known, to distinguish between the "Group velocity" and the "Phase velocity" of an individual wave in the group.

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* Communicated by Prof. S. Chapman, F.R.S.

It is not difficult to calculate these. We can take as a basis the ordinary electromagnetic equations, and no loss of generality will be occasioned by the choice of a simple plane wave, since the solutions are linear (when we neglect the effect of the magnetic field in the wave front) and any system of wave motion can be built up out of these waves.

We will take, therefore,

$$\operatorname{curl} \mathrm{E} = -\frac{\mu}{c}\frac{\partial \mathrm{H}}{\partial t}, \qquad \operatorname{curl} \mathrm{H} = \mathrm{K}\frac{\partial \mathrm{E}}{\partial t} + v\rho,$$

where ρ is the electrical density of the ions and v their velocity

$$\mathrm{E} = \mathrm{X}, \mathrm{Y}, \mathrm{Z}, \qquad \mathrm{H} = \alpha, \beta, \gamma.$$

Assume a plane wave propagated in the x direction, β and Z only existing; then

$$\frac{\partial \mathrm{Z}}{\partial x} = -\mu\frac{\partial \beta}{\partial t},$$

$$\frac{\partial \beta}{\partial x} = \mathrm{K}\frac{\partial \mathrm{Z}}{\partial t} + v\mathrm{N}e,$$

or

$$\frac{\partial^2 \mathrm{Z}}{\partial x^2} = \frac{\mu \mathrm{K}}{c^2}\frac{\partial^2 \mathrm{Z}}{\partial t^2} + \frac{\partial}{\partial t}\mathrm{N}ev, \quad \ldots\ldots \quad (1)$$

and the equation for v is given by

$$m\frac{\partial v}{\partial t} + fv = \mathrm{Z}e;$$

if we neglect effects due to collisions, then fv can be neglected in comparison with $m\frac{\partial v}{\partial t}$.

If the waves are periodic, p being 2π × frequency, the last equation may be put

$$impv = \mathrm{Z}e$$

(neglecting the term fv); on substituting for v in (1) we get V^2 the square of the phase velocity:

$$\mathrm{V}^2 = c^2 \frac{1}{\left(1 - \frac{\mathrm{N}e^2c}{mp^2}\right)}, \text{ where } \mu\mathrm{K} = 1,$$

or

$$\mathrm{V} = c\sqrt{1 + \frac{\lambda^2}{\lambda_1^2}}, \text{ where } \lambda_1^2 = \frac{4\pi^2 mc^2}{\mathrm{N}e^2},$$

or

$$\mathrm{V} = c\sqrt{1 + \frac{\kappa_1^2}{\kappa^2}}, \text{ where } \kappa = 2\pi/\lambda.$$

The group velocity

$$= \frac{\partial \kappa V}{\partial \kappa} = U = \frac{c}{\sqrt{1+\kappa_1^2/\kappa^2}},$$

$$\text{and} \qquad UV = c^2.$$

We can use an approximate method, due to Prof. Havelock, to determine the subsequent history of a sudden impulse or what he called a "limited initial disturbance." But it is possible, without the aid of an elaborate mathematical analysis, to obtain an idea of this.

Any impulse can be split up by the aid of Fourier's analysis into a "band of spectrum of all frequencies"; for an example, an impulse of the form $\frac{a^2}{a^2+t^2}$ is expressible as $\frac{1}{\pi}\int_0^{\infty} e^{-ap} \sin pt\, dp$, which shows that for all frequencies which are small compared with $1/a$ the intensity in the spectrum is nearly constant. In a linear dispersive medium each component of the "spectrum" is transmitted with its appropriate velocity, and the result will be that after a suitable interval, long or short according to the amount of "dispersion" in the medium, the various frequencies will be all separated out. Thus waves of length λ will be found after a time t in the neighbourhood of the distance tU_λ, where U_λ is the appropriate *group* velocity for this wave-length.

The group velocity is involved here, and not the phase velocity, because elementary analysis shows that a group of waves of the wave-length λ moves as a whole with the velocity U_λ, although the individual waves in the group move with the velocity V_λ, *i.e.* are continually moving through the group.

Now U_λ is small for large values of λ and increases as λ is decreased up to the limiting value c, the velocity of light, when $\lambda \rightarrow 0$. The short wave-lengths travel fastest and arrive first, and the long wave-lengths last.

To a stationary observer this appears as a note of rapidly decreasing frequency and bears a strong resemblance to the actual sounds heard.

It must be left to actual measurements and theoretical calculation to decide how close this resemblance is.

It is shown (Cambridge Tracts in Mathematics and Mathematical Physics, No. 17) by Prof. Havelock that the subsequent history of a limited initial disturbance can be calculated with a fair degree of accuracy from the formula :

$$y = \frac{1}{2\pi}\left\{\frac{2\pi}{t\left(\frac{\partial U}{\partial \kappa}\right)_0}\right\}^{1/2}\cos\{k_0(x-V_0t)\pm\pi/4\}, \quad . \quad . \quad (2)$$

where k_0 is expressed in terms of x and t by the formula

$$x-U_0t = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where U_0 in this case is

$$U_0=\frac{c}{\sqrt{1+\frac{\kappa_1^2}{\kappa^2}}}, \qquad \left(\frac{\partial U_0}{\partial\kappa}\right)=\frac{c}{\kappa^2}\frac{\kappa_1^2}{\kappa}\frac{1}{(1+\kappa_1^2/\kappa^2)^{3/2}}.$$

Expressing these quantities in terms of x and t by relation (3) we get the following expression for y :

$$y=\frac{1}{2\pi}\left\{\frac{2\pi\kappa_1}{ct\left\{1-\frac{x^2}{c^2t^2}\right\}^{3/2}}\right\}^{1/2}\cos\{\kappa_1(x^2-c^2t^2)^{1/2}+\pi/4\}.$$

This expression represents a disturbance of varying frequency, the high frequency starting first and tailing down to a low frequency as time elapses.

Limiting Frequency.

When ct is large compared with x, *i.e.* if we consider the tail-end of the disturbance, we get approximately

$$y=\frac{1}{2\pi}\left\{\frac{2\pi\kappa_1}{ct}\right\}^{1/2}\cos(\kappa_1 ct),$$

which represents a disturbance of constant frequency $\frac{\kappa_1 c}{2\pi}$, and of gradually decreasing amplitude.

This constant limiting frequency is another point of resemblance with actual fact, and the equation

$$n_1=\frac{\kappa_1 c}{2\pi}=\frac{1}{2\pi}\left(\frac{e^2N}{m}\right)^{1/2}$$

gives values of N, the number of ions per c.c., for different types of ions.

If we assume for instance that the ions are electrons, and it will be seen that they contribute chiefly to the value of Ne, we get

$$n=\frac{1}{2\pi}(1\cdot7\times10^7)(eN)^{1/2};$$

so that if $n=300$ we get eN of the order $2\cdot2\times10^{-21}$, which is of the order of 1 ion per c.c.

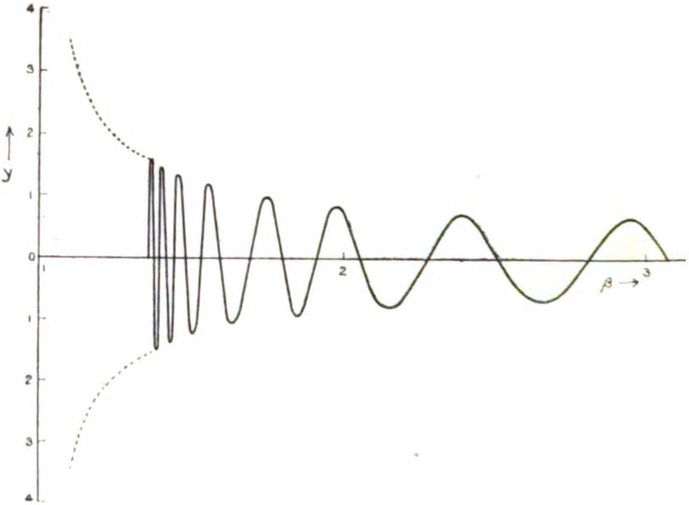
The attached curve, fig. 1, shows y as a function of $ct/x=\beta$ with $\kappa_1 x=3\pi$ approx., *i. e.* at a distance where the component frequencies have been well separated out.

Fig. 1.

Form of Disturbance computed from the Formula

$$y=\frac{1}{2\pi}\left\{\frac{\frac{\kappa_1}{x}}{\beta\left(1-\frac{1}{\beta^2}\right)^{3/2}}\right\}^{1/2}\cos\left\{\kappa_1 x(1-\beta^2)^{1/2}+\pi/4\right\}.$$

$$\beta=\frac{ct}{x},\qquad \kappa_1 x=3\pi \text{ approx.}$$



The part in the neighbourhood of $x=ct$, *i. e.* the head of the disturbance, is probably inaccurate and anyhow depends on the shape and thickness of the original impulse. It is therefore shown dotted, and only the envelope of the waves given.

An attempt to get a more accurate representation than the one given by the approximate formula (fig. 1) is developed here, and it will be found that when ct is large compared with x the original formula is approximately correct.

If V is the phase velocity corresponding to the wavelength λ and $\kappa=\frac{2\pi}{\lambda}$, then we can express the subsequent history of a pulse $\frac{a^2}{a^2+x^2}$ in the form

$$y=\text{a real part of }\frac{1}{\pi}\int_0^\infty e^{-a\kappa+i\kappa(x-\mathrm{V}t)}d\kappa, \quad . \quad . \quad (4)$$

where V is expressible in terms of κ in the form

$$V = c\sqrt{1+\kappa_1^2/\kappa^2}$$

so that $$\kappa V = c^2\sqrt{\kappa^2+\kappa_1^2};$$

we have therefore to evaluate the integral

$$y = \frac{1}{\pi}\int_0^\infty d\kappa e^{i\kappa(x+ia)-i\sqrt{\kappa^2+\kappa_1^2}ct}, \quad . \quad . \quad . \quad (5)$$

or $$\frac{1}{\pi}\int_0^\infty d\kappa e^{i\kappa x_1-i\sqrt{\kappa^2+\kappa_1^2}ct},$$

where $x_1=x+ia$.

Let $$U = \kappa/\kappa_1 \quad \text{and} \quad U = \sinh v,$$

then $$y = \frac{\kappa_1}{\pi}\int_0^\infty e^{i\kappa_1 x_1 \sinh v - i\kappa_1 ct \cosh v} \cosh v\, dv.$$

Now let

$$\begin{aligned} ct &= R\cosh\phi, \\ x_1 &= R\sinh\phi, \end{aligned} \quad R^2 = (c^2t^2-x_1^2), \quad . \quad . \quad (6)$$

$$i\kappa_1(x_1\sinh v - ct\cosh v) = -iR\kappa_1\cosh(v-\phi);$$

so that if $w=v-\phi$

$$y = \frac{\kappa_1}{\pi}\int_{-\phi}^{+\infty} e^{-i\kappa_1 R\cosh w} \cosh(w+\phi)\, dw$$

$$= \frac{\kappa_1}{\pi}\int_{-\phi}^{\infty} \cosh\phi\, e^{-i\kappa_1 R\cosh w} \cosh w\, dw$$

$$+ \frac{\kappa_1}{\pi}\int_{-\phi}^{+\infty} \sinh\phi\, e^{-i\kappa_1 R\cosh w} \sinh w\, dw.$$

The latter term can be integrated immediately; it is

$$\frac{\sinh\phi}{\pi R} \cdot e^{i\kappa_1 R\cosh\phi},$$

and taking (6) into account this becomes

$$\frac{1}{\pi}\frac{x_1}{c^2t^2-x_1^2}e^{i\kappa_1 ct}.$$

It should be observed that the *Real Part of* $-iR$ *is Negative.*

The other term,

$$\frac{\kappa_1}{\pi}\int_{-\phi}^{\infty} \cosh\phi\, e^{-i\kappa_1 R\cosh w} \cosh w\, dw$$

$$= \frac{\kappa_1}{\pi}\int_{-\phi}^{0} \cosh\phi\, e^{-i\kappa_1 R\cosh w} \cosh w\, dw$$

$$+ \frac{\kappa_1}{\pi}\int_{0}^{\infty} \cosh\phi\, e^{-i\kappa_1 R\cosh w} \cosh w\, dw.$$

This latter term is $\frac{\kappa_1}{\pi}\cos\phi\,\mathrm{K}_1(i\kappa_1\mathrm{R})$ where $\mathrm{K}_1(x)$ is the second Bessel Function of order 1 when the real part of $-i\kappa_1\mathrm{R}$ is negative; and if ϕ is small, i.e. $ct \geqslant x$, the first term is nearly zero.

The total is therefore

$$\frac{1}{2\pi}\sqrt{\frac{2\pi\kappa_1}{ct\left(1-\frac{x^2}{c^2t^2}\right)^{3/2}}}\cos\left\{\kappa_1(x_1^2-c^2t^2)^{1/2}\right\}$$

$$+\frac{1}{\pi}\frac{x_1}{(c^2t^2-x_1^2)}\cos\kappa_1ct+\frac{\kappa_1}{\pi}\int_{-\phi}^{0}\cosh\phi\, e^{-i\kappa_1\mathrm{R}\cosh w}\cosh w\,dw,$$

on replacing $\mathrm{K}_1(i\kappa_1\mathrm{R})$ by its asymptotic value. This reduces to the former value (2) when ct is large compared with x.

When x is approximately equal to ct, ϕ is always a finite quantity when "a" is finite, for

$$\cosh\phi=\frac{ct}{\sqrt{2aix}}\text{ approx. if }\phi=p+iq\,;$$

then

$$\tanh p=1-\frac{2ax}{ax+c^2t^2}\text{ approx. and }p\to\infty,\quad a\to 0,$$

$$\tan q=1+\frac{2ax}{ax+c^2t^2}\quad\text{,,}\quad q\to\frac{\pi}{4},\quad\text{,,}$$

If we integrate from $-iq-p$ to $-p$ and from $-p$ to 0 when a is small, the latter part, *i.e.* $\int_{-p}^{0}$, becomes very nearly

$$\kappa_1\frac{\cosh\phi}{\pi}\mathrm{K}_1(i\kappa_1\mathrm{R}),$$

and the former part is negligible except in the neighbourhood of $w=-\phi$, and tends to zero when ct is large.

The total when ct and x are large and nearly equal is

$$\frac{2\kappa_1\cosh\phi}{\pi}(\mathrm{K}_1(i\kappa_1\mathrm{R}))+\frac{1}{\pi}\frac{x_1}{c^2t-x_1}\cos\kappa_1ct.$$

This shows that the approximate form is only accurate when ct is large compared with x, but the conclusion that a limiting frequency $\frac{\kappa_1c}{2\pi}$ is reached is shown to be accurately true. A measurement of this frequency should therefore be of value in determining the constants of the conductive medium.

The fact that these peculiar types of disturbance occur almost entirely at night suggest that they have their origin in the permanent auroral conducting layer, and not in the lower layer ionized in the daytime. The value of N*e* should therefore apply to this low-pressure region, and not to the relatively high-pressure zone where the attenuation of radio waves is so high as to eliminate all types of disturbance originating above it.

As we have seen, the approximate values of N*e* for electrons are of the order 2×10^{-21} to 2×10^{-22}, and for α-particles $2{\cdot}7\times 10^{-18}$ to $2{\cdot}7\times 10^{-19}$. This is of the order of one electrified particle per c.c. It is very difficult to say in what region of the auroral layer these impulses originate. If we assume the outside, the waves have to pass right through the medium and the value of N*e* is probably an average of the quantity throughout the layer.

If, on the other hand, we assume that the impulses are produced by the sudden stoppage of groups of particles at the bottom edge of the layer, the value of N*e* should be that corresponding to the lower fringe of the layer.

If the conductivity is known, as well as N*e*, we can estimate T, the mean free life of an electron in the region where the impulses originate. For the conductivity σ is $\mathrm{N}e.\frac{e}{m}\mathrm{T}$, and when N*e*, $\frac{e}{m}$, and σ are known, T can be deduced. The average conductivity has been estimated by Schuster (in his theory of the diurnal variations of the earth's magnetism) to be of the order 10^{-14} c.g.s. units if the layer is assumed to be 300 km. thick. S. Chapman has estimated that the total conduction is equivalent to a layer of copper 1 metre thick, but the magnetic evidence is insufficient to give the actual conductivity at any point in the layer. The evidence afforded by the attenuation of radio waves at night is the most relevant. Unfortunately, the attenuation constant does not determine an unique value of the conductivity; two values are possible, *i.e.* approx. $\frac{1}{1{\cdot}7}\times 10^{-14}$ and $\frac{1}{3}\times 10^{-19}$. These values refer to the effective conductivities for high frequencies (n in the neighbourhood of 10^4), which are derived from the steady current conductivities according to the relation

$$\sigma=\sigma_0\Big/\sqrt{1+\left(\frac{2\pi\mathrm{T}}{t}\right)^2}\quad\text{or}\quad\sigma=\frac{\mathrm{N}e^2\mathrm{T}}{m}\Big/\sqrt{1+\left(\frac{2\pi\mathrm{T}}{t}\right)^2},$$

where t is the time period of the electromagnetic waves and T has the same significance as before.

Equating this to 4.10^{-19}, Ne to 2×10^{-22}, and t to 10^{-4} $e/m = 1{\cdot}77\times10^{7}$, we have

$$\frac{2\pi T}{t}\Big/\sqrt{1+\left(\frac{2\pi T}{t}\right)^{2}} = \frac{10^{-19}\times 2\pi\times 10^{7}}{3\times 1{\cdot}77\times 10^{7}\times 2\times 10^{-22}}.$$

or

$$\left(\frac{2\pi T}{t}\right)^{2}\Big/ 1+\left(\frac{2\pi T}{t}\right)^{2} = 0{\cdot}35\,;$$

$$i.e.\quad \frac{2\pi T}{t} = 0{\cdot}89,$$

$$T = \frac{1}{70{,}500}\ \text{approx.}$$

If, on the other hand, we use the other possible value of σ, *i.e.* $\frac{1}{1{\cdot}7}\times 10^{-14}$, the equation $Ne\frac{e}{m}T\Big/\sqrt{1+\left(\frac{2\pi T}{t}\right)^{2}} = \sigma$ cannot be satisfied by any real value of T; for we get, when $x = \left(\frac{2\pi T}{t}\right)$,

$$\frac{x}{\sqrt{1+x^{2}}} = \frac{10^{-14}\times 2\pi\times 10^{4}}{1{\cdot}7\times 1{\cdot}77\times 10^{7}\times 2\times 10^{-22}} = \frac{\pi\times 10^{6}}{1{\cdot}7\times 1{\cdot}77} > 1$$

and the relation cannot be satisfied by any real value of T. The calculation therefore suggests that ρ is of the order 3×10^{19} and $T=\frac{1}{70{,}000}$ if we assume that the impulses, which give rise to the musical strays, originate in the lower fringe of the conducting layer which is responsible for the attenuation of radio waves at night.

In confirmation of this we have further evidence derived from this source. With resistivities as high as this, the attenuation takes the form $e^{-\frac{2\pi}{\rho_n}x}$, where ρ_n is the resistivity at the frequency n. Now $\rho_n = \rho_0\sqrt{1+\left(\frac{2\pi T}{t}\right)^{2}}$, where ρ_0 is the resistivity for sufficiently low frequencies, and T and t have the same significance as before. The attenuation constant should therefore be of the form:

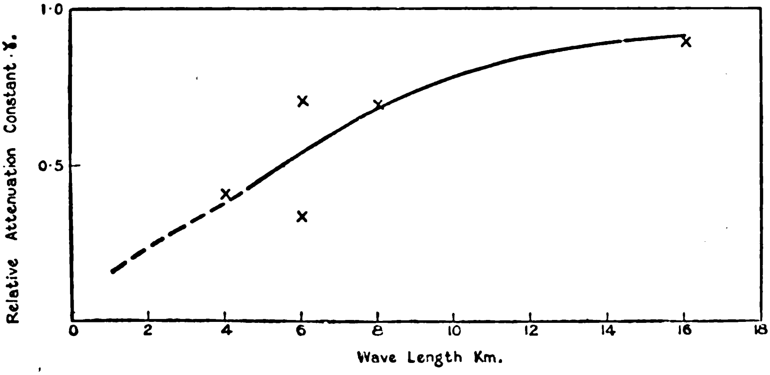
$$\frac{A}{\sqrt{1+p^{2}/p_0^{\,2}}},\ \text{where}\ p = 2\pi n,\ p_0 = \frac{1}{T}.$$

The curve (fig. 2), derived from approximate data, shows that this is roughly the case. Calculating T from the curve we get $T = \frac{1}{100{,}000}$, which does not differ greatly from the previous value. The analytical expression (fig. 2) takes no account of the attenuation which must occur in the dispersive medium by the intercollision of the free electrons and ions.

I hope in a later paper to show that the attenuation introduced by this dissipation does not materially influence the results obtained here. The approximate results indicate that the tail-end of the disturbance is most attenuated, but the fact that the limiting frequency is approached fairly closely in practice shows that this attenuation cannot be excessive.

Fig. 2.

Approximate Relative Values of Night Attenuation.



This result should lead to an independent estimate of T, which should act as a check on the theory.

Recently Sir Joseph Larmor has developed a theory of radio transmission in which the observed bending of the rays round the earth is attributed to the same mechanism as is assumed in this paper, and the results he arrives at are in substantial agreement with those obtained here.

In particular he arrives at the result that N, the number of electrons per c.c., need not exceed 1, which is in good agreement with the results obtained here.

Again, the value $T=10^{-5}$ is in agreement with Larmor's value.

For the value T_0 between actual encounters is estimated by him to be $\frac{1}{30}\ 10^{-5}$, but from the mode of origin of T this quantity is obviously the time between encounters which involve a large dissipation of energy, and, as he has pointed out, laboratory experience has shown that an electron can pass through an atom with but slight derangement of its motion in all but exceptional cases, implying that T is large compared with T_0 and may well be 30 times as great.

This factor would bring the two determinations of T into agreement.

CXXVII. *Determination of the Minimum Plane in Four-Dimensional Space with respect to a System of Non-Coplanar Points.* *By* H. S. Uhler, *B.A.*, *Ph.D.*, *Associate Professor of Physics, Yale University* *.

Synopsis.—The material presented after the introductory remarks will comprise in order the following items: (*a*) derivation of a general formula for the length of the perpendicular dropped from a point to a plane in four-space; (*b*) use of this distance formula in the Method of Least Squares; (*c*) proof of the significant fact that the complete sextic equation which arises in part (*b*) can always be reduced to a cubic; and (*d*) evaluation of a numerical illustration.

Introduction.—The primary object of this paper is to derive a set of exact formulas for the determination of the position of a plane in four-dimensional space, such that the sum of the squares of the lengths of the perpendiculars dropped from any (large enough) number of given points upon the plane shall be a minimum. In non-geometrical language, the problem may be interpreted as that of the determination of the most probable values of the coefficients in two appropriate linear equations involving four variables with respect to the observational data of a given system which does not satisfy any pair of linear equations. The error curve is assumed to be the normal distribution of Gauss, and the variables are treated as having equal mathematical weights. The condition stated last does not limit the generality of the solution, since for unequal weights it is always possible to transform the coordinates to a new set of variables having equal weights, to solve the transformed problem, and finally to return to the original set †.

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* Communicated by Prof. W. F. G. Swann.

† H. S. Uhler, "Method of Least Squares and Curve Fitting." Journ. Opt. Soc. Amer. and Rev. Sci. Insts., vol. vii. no. 11, p. 1043 (1923).

THE present paper supplements one written by Karl Pearson entitled "On Lines and Planes of Closest Fit to Systems of Points in Space" [this Magazine, 6th series, vol. ii. pp. 559--572 (1901)]. By the term "plane" Pearson means a linear space having $n-1$ degrees of freedom in n-dimensional flat space. Hence, for $n=4$ he has solved the cases of the hyperplane (3-space) and the straight line. Both papers contain material which may be useful in the theory of correlation. Pearson's "standard-deviations" σ_w, σ_x, σ_y, σ_z, and the σ's first introduced below in equation (19) may be converted into one another by the relations

$$\sigma_w = \frac{\sqrt{\sigma_{11}}}{\kappa}, \quad \sigma_x = \frac{\sqrt{\sigma_{22}}}{\kappa}, \quad \sigma_y = \frac{\sqrt{\sigma_{33}}}{\kappa}, \quad \sigma_z = \frac{\sqrt{\sigma_{44}}}{\kappa}.$$

Similarly his "correlation coefficients" or r's may be calculated from the σ's of the present article by means of the generally irrational equations

$$r_{wx} = \frac{\sigma_{12}}{\sqrt{\sigma_{11}\sigma_{22}}}, \quad r_{wy} = \frac{\sigma_{13}}{\sqrt{\sigma_{11}\sigma_{33}}}, \quad \ldots, \quad r_{yz} = \frac{\sigma_{34}}{\sqrt{\sigma_{33}\sigma_{44}}}.$$

(a) Let the non-homogeneous equations of the hyperplanes which intersect in the plane and determine it be

$$\left.\begin{aligned} \alpha w + \beta x + \gamma y + \delta z + \epsilon = 0, \\ \alpha' w + \beta' x + \gamma' y + \delta' z + \epsilon' = 0, \end{aligned}\right\} \quad . \quad . \quad . \quad (1)$$

where w, x, y, and z are the rectangular coordinates of any point in the plane. Let M denote the array or matrix

$$\begin{matrix} \alpha & \beta & \gamma & \delta \\ \alpha' & \beta' & \gamma' & \delta', \end{matrix}$$

the rank of which will be assumed to be two. Let Δ symbolize the distance between the point (w', x', y', z') which does not lie in the plane represented by equations (1) and the point (w, x, y, z). Then

$$(w-w')^2 + (x-x')^2 + (y-y')^2 + (z-z')^2 - \Delta^2 = 0. \quad . \quad (2)$$

The coordinates w, x, y, and z are to be varied in such a manner as to make Δ a minimum subject to the conditions imposed by equations (1). In Euclidean space this process will adjust the straight line joining the points (w, x, y, z) and (w', x', y', z') to perpendicularity to the plane. Hence differentiate equations (2) and (1), and put $d\Delta=0$ to obtain

$$\left.\begin{array}{llll}(w-w')dw+(x-x')dx+(y-y')dy+(z-z')dz=0,\\ \alpha\, dw+\quad \beta\, dx+\quad \gamma\, dy+\quad \delta\, dz=0,\\ \alpha' dw+\quad \beta' dx+\quad \gamma' dy+\quad \delta' dz=0.\end{array}\right\} . \quad (3)$$

Following Lagrange's method of undetermined factors, multiply the first, the second, and the third equation of set (3) respectively by m, $-\mu$, $-\mu'$, then add, and equate to zero the resulting polynomial coefficients of the differentials dw, dx, dy, and dz to get

$$\left.\begin{array}{l}(w-w')m-\alpha\mu-\alpha'\mu'=0,\\ (x-x')m-\beta\mu-\beta'\mu'=0,\\ (y-y')m-\gamma\mu-\gamma'\mu'=0,\\ (z-z')m-\delta\mu-\delta'\mu'=0.\end{array}\right\} \quad . \quad . \quad . \quad . \quad (4)$$

Let F and F' denote the values obtained by substituting in equations (1) the fixed coordinates of the point (w', x', y', z') for those of the variable point (w, x, y, z); that is

$$F \equiv \alpha w'+\beta x'+\gamma y'+\delta z'+\epsilon$$

and $$F' \equiv \alpha' w'+\beta' x'+\gamma' y'+\delta' z'+\epsilon'.$$

Now multiply the first equation of set (1), and the successive equations of set (4) read downward by m, $-\alpha$, $-\beta$, $-\gamma$, $-\delta$ respectively, and add the products thus formed to find the second equation of set (5) below. In like manner multiply the second equation of set (1) and equations (4) in order by m, $-\alpha'$, $-\beta'$, $-\gamma'$, $-\delta'$, and add the results to get the third equation of group (5). The first equation of this group is the sum of the products obtained by multiplying equation (2) and equations (4) respectively by $-m$, $w-w'$, $x-x'$, $y-y'$, and $z-z'$.

$$\left.\begin{array}{l}\Delta^2 m+F\mu+F'\mu'=0,\\ Fm+(\alpha^2+\beta^2+\gamma^2+\delta\ )\mu+(\alpha\alpha'+\beta\beta'+\gamma\gamma'+\delta\delta')\mu'=0,\\ F'm+(\alpha'\alpha+\beta'\beta+\gamma'\gamma+\delta'\delta)\mu+(\alpha'^2+\beta'^2+\gamma'^2+\delta'^2)\mu'=0,\end{array}\right\} \quad . \quad . \quad . \quad (5)$$

A necessary and sufficient condition that equations (5) may have a solution other than $m=\mu=\mu'=0$ is

$$\begin{vmatrix}\Delta_0^2, & F\quad, & F'\\ F, & \alpha^2+\beta^2+\gamma^2+\delta^2, & \alpha\alpha'+\beta\beta'+\gamma\gamma'+\delta\delta'\\ F', & \alpha'\alpha+\beta'\beta+\gamma'\gamma+\delta'\delta, & \alpha'^2+\beta'^2+\gamma'^2+\delta'^2\end{vmatrix}=0. \quad (6)$$

where the subscript zero emphasizes the fact that the value of Δ derived from the solution of equation (6) is a minimum.

For the present purposes it is necessary to expand the above bordered symmetrical determinant. This may be accomplished in the following manner. Let this determinant be written as $D\Delta_0^2 - N$. By compounding M with its conjugate

$$\begin{matrix} \alpha & \alpha' \\ \beta & \beta' \\ \gamma & \gamma' \\ \delta & \delta', \end{matrix}$$

it is seen at once that

$$\left.\begin{aligned} D = (\alpha\beta' - \alpha'\beta)^2 + (\alpha\gamma' - \alpha'\gamma)^2 + (\alpha\delta' - \alpha'\delta)^2 \\ + (\beta\gamma' - \beta'\gamma)^2 + (\beta\delta' - \beta'\delta)^2 + (\gamma\delta' - \gamma'\delta)^2 \end{aligned}\right\} \quad . \quad . \quad . \quad (7)$$

By applying Cauchy's theorem* for the expansion of a bordered determinant D as a homogeneous function of the bordering constituents it is readily found that

$$\begin{aligned} N = (\alpha F' - \alpha' F)^2 + (\beta F' - \beta' F)^2 \\ + (\gamma F' - \gamma' F)^2 + (\delta F' - \delta' F)^2. \quad . \quad (8) \end{aligned}$$

Let

$$\begin{aligned} l &\equiv (\alpha\beta' - \alpha'\beta) \,/\, \sqrt{D}, & p &\equiv (\beta\gamma' - \beta'\gamma) \,/\, \sqrt{D}, \\ m &\equiv (\alpha\gamma' - \alpha'\gamma) \,/\, \sqrt{D}, & q &\equiv (\beta\delta' - \beta'\delta) \,/\, \sqrt{D}, \\ n &\equiv (\alpha\delta' - \alpha'\delta) \,/\, \sqrt{D}, & r &\equiv (\gamma\delta' - \gamma'\delta) \,/\, \sqrt{D}. \end{aligned}$$

Then equation (7) becomes

$$l^2 + m^2 + n^2 + p^2 + q^2 + r^2 = 1, \quad . \quad . \quad . \quad . \quad (9)$$

and the identity

$$\begin{aligned} (\alpha\beta' - \alpha'\beta)(\gamma\delta' - \gamma'\delta) - (\alpha\gamma' - \alpha'\gamma)(\beta\delta' - \beta'\delta) \\ + (\alpha\delta' - \alpha'\delta)(\beta\gamma' - \beta'\gamma) = 0 \end{aligned}$$

changes to

$$lr - mq + np = 0. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Substitution in equation (8) of the expressions for F and F'' given just after equations (4) leads to

$$\begin{aligned} \Delta_0^2 = N/D = [lx' + my' + nz' + (\alpha\epsilon' - \alpha'\epsilon)/\sqrt{D}]^2 + [py' + qz' - lw' \\ + (\beta\epsilon' - \beta'\epsilon)/\sqrt{D}]^2 + [rz' - mw' - px' + (\gamma\epsilon' - \gamma'\epsilon)/\sqrt{D}]^2 \\ + [-nw' - qx' - ry' + (\delta\epsilon' - \delta'\epsilon)\,/\,\sqrt{D}]^2 \quad . \quad . \quad . \quad . \quad (11) \end{aligned}$$

Expression (11) may be changed to the form best adapted to the main problem by letting the given point

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* R. F. Scott & G. B. Mathews, 'Theory of Determinants,' p. 47, § 25.

$(\bar{w}, \bar{x}, \bar{y}, \bar{z})$ lie in the plane. Then

$$(\alpha\epsilon'-\alpha'\epsilon) / \sqrt{D} = -l\bar{x}-m\bar{y}-n\bar{z},$$
$$(\beta\epsilon'-\beta'\epsilon)/ \sqrt{D} = -p\bar{y}-q\bar{z}+l\bar{w},$$
$$(\gamma\epsilon'-\gamma'\epsilon) / \sqrt{D} = -r\bar{z}+m\bar{w}+p\bar{x},$$
$$(\delta\epsilon'-\delta'\epsilon) / \sqrt{D} = n\bar{w}+q\bar{x}+r\bar{y}.$$

$$\Delta_0^2 = (nW'+qX'+rY')^2+(lX'+mY'+nZ')^2 + (pY'+qZ'-lW')^2+(-rZ'+mW'+pX')^2, \quad (12)$$

where

$$W' \equiv \bar{w}-w', \quad X' \equiv \bar{x}-x', \quad Y' \equiv \bar{y}-y', \quad Z' \equiv \bar{z}-z'.$$

Formula (12) gives directly the square of the length of the perpendicular dropped from the point (w', x', y', z') to the plane represented by any two of the equations of set (13).

$$\left.\begin{aligned} E_1 &\equiv lx+my+nz-(l\bar{x}+m\bar{y}+n\bar{z}) = 0, \\ E_2 &\equiv -lw+py+qz-(-l\bar{w}+p\bar{y}+q\bar{z}) = 0, \\ E_3 &\equiv mw+px-rz-(m\bar{w}+p\bar{x}-r\bar{z}) = 0, \\ E_4 &\equiv nw+qx+ry-(n\bar{w}+q\bar{x}+r\bar{y}) = 0. \end{aligned}\right\} . \quad (13)$$

These equations may be looked upon as having been derived from equations (1) by the successive elimination of w, x, y, and z respectively. The four equations of set (13) are equivalent to only two independent equations as a consequence of condition (10). For example,

$$nE_2 = qE_1 - lE_4 \quad \text{and} \quad nE_3 = -rE_1 + mE_4.$$

From a slightly different point of view, a necessary and sufficient condition that the following group of homogeneous linear equations (which are those of set (13) re-written)

$$\left.\begin{aligned} lX+mY+nZ &= 0, \\ -lW \qquad +pY+qZ &= 0, \\ -mW-pX \qquad +rZ &= 0, \\ -nW-qX-rY \qquad &= 0, \end{aligned}\right\}$$

shall have a solution other than $W=X=Y=Z=0$ is the vanishing of the determinant of the coefficients. This determinant is skew-symmetrical, its order is even, and it equals $(lr-mq+np)^2$. Hence equation (10) is the required condition.

For sake of completeness attention should be called to the fact that, if desired, the coordinates w, x, y, z of the foot of the perpendicular dropped from the point (w', x', y', z') upon the plane may be obtained by eliminating m, μ, and μ' from the last two equations of set (5) and each of equations (4). The formulæ obtained may be written:

$$\left.\begin{aligned} w&=w'+[\ \ l(\beta F'-\beta'F)+m(\gamma F'-\gamma'F)+n(\delta F'-\delta'F)]\,/\,\sqrt{D},\\ x&=x'+[-l(\alpha F'-\alpha'F)+p(\gamma F'-\gamma'F)+q(\delta F'-\delta'F)]\,/\,\sqrt{D},\\ y&=y'+[-m(\alpha F'-\alpha'F)-p(\beta F'-\beta'F)+r(\delta F'-\delta'F)]\,/\,\sqrt{D},\\ z&=z'+[-n(\alpha F'-\alpha'F)-q(\beta F'-\beta'F)-r(\gamma F'-\gamma'F)]\,/\,\sqrt{D},\end{aligned}\right\}\quad(14)$$

or

$$\left.\begin{aligned} w&=w'-lE'_2+mE'_3+nE'_4,\\ x&=x'+lE'_1+pE'_3+qE'_4,\\ y&=y'+mE'_1+pE'_2+rE'_4,\\ z&=z'+nE'_1+qE'_2-rE'_3,\end{aligned}\right\}\ \ .\ \ .\ \ .\quad(15)$$

where

$$\begin{aligned} E'_1&\equiv\ \ lX'+mY'+nZ',\\ E'_2&\equiv-lW'+pY'+qZ',\\ E'_3&\equiv\ \ mW'+pX'-rZ',\\ E'_4&\equiv\ \ nW'+qX'+rY'.\end{aligned}$$

Obviously it should be possible to deduce formula (12) by substituting in equation (2) the expressions given by equations (15) for $w-w'$, $x-x'$, $y-y'$, and $z-z'$. As a matter of fact, this substitution, followed by appropriate use of condition (9), leads to

$$\begin{aligned}&(E'_1)^2+(E'_2)^2+(E'_3)^2+(E'_4)^2-\triangle_0^2\\ &\quad=(-pE'_1+mE'_2+lE'_3)^2+(-qE'_1+nE'_2+lE'_4)^2\\ &\qquad+(rE'_1+nE'_3-mE'_4)^2+(rE'_2+qE'_3-pE'_4)^2.\quad(16)\end{aligned}$$

Replacing E'_1, E'_2, E'_3, and E'_4 in the parentheses of equation (16) by their respective values in terms of W', X', Y', and Z', and then making use of condition (10), it is found that the right-hand member of equation (16) vanishes, thus leaving formula (12). Nevertheless, the method given first is to be preferred, since it leads directly to formula (6) and since it is susceptible of generalization to n-dimensional linear space.

(*b*) The ground is now prepared for the solution of the main problem of the paper, which belongs to the domain of the Method of Least Squares, namely: to determine a two-dimensional plane in four-space so as to make the sum of the squares of the lengths of the perpendiculars dropped upon the plane from any (sufficiently large) number of given points a minimum.

Let the number of points outside the plane be κ (>3), and let the ith point be symbolized by (w_i, x_i, y_i, z_i), where $i=1, 2, \ldots, \kappa$. Also, let ϕ denote the sum of the squares of the perpendiculars in question. Then, by formula (12),

$$\phi \equiv \sum_1^\kappa \Delta_i^2 = \sum_1^\kappa [(nW_i+qX_i+rY_i)^2+(lX_i+mY_i+nZ_i)^2 + (pY_i+qZ_i-lW_i)^2+(-rZ_i+mW_i+pX_i)^2], \quad (17)$$

where

$$W_i\equiv \bar{w}-w_i, \quad X_i\equiv \bar{x}-x_i, \quad Y_i\equiv \bar{y}-y_i, \quad Z_i\equiv\bar{z}-z_i.$$

ϕ is to be a minimum with respect to the ten quantities $\bar{w}, \bar{x}, \bar{y}, \bar{z}, l, m, n, p, q, r$.

$\dfrac{\partial\phi}{\partial\bar{w}}=0$, $\dfrac{\partial\phi}{\partial\bar{x}}=0$, $\dfrac{\partial\phi}{\partial\bar{y}}=0$, $\dfrac{\partial\phi}{\partial\bar{z}}=0$ lead to the following equations in the order given:—

$$\left.\begin{aligned}
(l^2+m^2+n^2)W''+(mp+nq)X''-(lp-nr)Y''-(lq+mr)Z''&=0,\\
(mp+nq)W''+(l^2+p^2+q^2)X''+(lm+qr)Y''+(ln-pr)Z''&=0,\\
-(lp-nr)W''+(lm+qr)X''+(m^2+p^2+r^2)Y''+(mn+pq)Z''&=0,\\
-(lq+mr)W''+(ln-pr)X''+(mn+pq)Y''+(n^2+q^2+r^2)Z''&=0,
\end{aligned}\right\} \quad (18)$$

where

$$W''\equiv\bar{w}-(\Sigma w)/\kappa, \quad X''\equiv\bar{x}-(\Sigma x)/\kappa, \quad Y''\equiv\bar{y}-(\Sigma y)/\kappa, \quad Z''\equiv\bar{z}-(\Sigma z)/\kappa.$$

Equations (18) are always satisfied when

$$W''=X''=Y''=Z''=0,$$

that is, when

$$\bar{w}=(\Sigma w)/\kappa, \quad \bar{x}=(\Sigma x)/\kappa, \quad \bar{y}=(\Sigma y)/\kappa, \quad \bar{z}=(\Sigma z)/\kappa;$$

hence the theorem: The minimum (or maximum) plane always passes through the centroid of the set of given points (w_i, x_i, y_i, z_i).

Substituting the values of $\bar{w}, \bar{x}, \bar{y}, \bar{z}$ in equation (17), squaring the parenthetical expressions, and performing the remaining summations with respect to the subscript i gives

$$\begin{aligned}\theta = (\sigma_{11}+\sigma_{22})l^2 &+ (\sigma_{11}+\sigma_{33})m^2 + (\sigma_{11}+\sigma_{44})n^2 + (\sigma_{22}+\sigma_{33})p^2 \\ &+ (\sigma_{22}+\sigma_{44})q^2 + (\sigma_{33}+\sigma_{44})r^2 + 2\sigma_{23}lm + 2\sigma_{24}ln \\ &- 2\sigma_{13}lp - 2\sigma_{14}lq + 2\sigma_{34}mn + 2\sigma_{12}mp - 2\sigma_{14}mr \\ &+ 2\sigma_{12}nq + 2\sigma_{13}nr + 2\sigma_{34}pq - 2\sigma_{24}pr + 2\sigma_{23}qr, \quad . \quad (19)\end{aligned}$$

where

$$\begin{aligned}&\theta \equiv \kappa\phi, \quad \sigma_{11} \equiv \kappa\Sigma(w^2) - (\Sigma w)^2, \quad \sigma_{22} \equiv \kappa\Sigma(x^2) - (\Sigma x)^2, \ldots, \\ &\sigma_{12} \equiv \kappa\Sigma(w_i x_i) - (\Sigma w)(\Sigma x), \ldots, \\ &\sigma_{34} \equiv \kappa\Sigma(y_i z_i) - (\Sigma y)(\Sigma z)\ ; \qquad \sigma_{ij} = \sigma_{ji}.\end{aligned}$$

A σ having equal subscripts is essentially positive for real values of the coordinates, since

$$\kappa\Sigma(t^2) - (\Sigma t)^2 = \Sigma(t_i - t_j)^2, \quad i < j.$$

Differentiating equations (19), (10), and (9), and putting $d\theta = 0$ leads to

$$\left.\begin{array}{l} B_1 dl + B_2 dm + B_3 dn + B_4 dp + B_5 dq + B_6 dr = 0, \\ r dl - q dm + p dn + n dp - m dq + l dr = 0, \\ l dl + m dm + n dn + p dp + q dq + r dr = 0, \end{array}\right\} \quad (20)$$

where

$$\begin{array}{llllll} \sigma_{11}+\sigma_{22})l & +\sigma_{23}m & +\sigma_{24}n & -\sigma_{13}p & -\sigma_{14}q, & \\ \sigma_{23}l & +(\sigma_{11}+\sigma_{33})m & +\sigma_{34}n & +\sigma_{12}p & & -\sigma_{14}r, \\ \sigma_{24}l & +\sigma_{34}m & +(\sigma_{11}+\sigma_{44})n & & +\sigma_{12}q & +\sigma_{13}r, \\ -\sigma_{13}l & +\sigma_{12}m & & +(\sigma_{22}+\sigma_{33})p & +\sigma_{34}q & -\sigma_{24}r, \\ -\sigma_{14}l & & +\sigma_{12}n & +\sigma_{34}p & +(\sigma_{22}+\sigma_{44})q & +\sigma_{23}r, \\ & -\sigma_{14}m & +\sigma_{13}n & -\sigma_{24}p & +\sigma_{23}q & +(\sigma_{33}+\sigma_{44})r. \end{array} \quad . \quad . \quad . \quad (21)$$

Multiply the first, second, and third equations of set (20) by 1, $-\xi$, and $-\eta$ respectively, add the products, and equate to zero the complete coefficients of the six differentials to obtain

$$\left.\begin{array}{ll} r\xi + l\eta = B_1, & n\xi + p\eta = B_4, \\ -q\xi + m\eta = B_2, & -m\xi + q\eta = B_5, \\ p\xi + n\eta = B_3, & l\xi + r\eta = B_6. \end{array}\right\} \quad . \quad . \quad . \quad (22)$$

Form the sum of the products obtained by multiplying each equation of set (22) by the respective coefficient of ξ to find, by the aid of expressions (21), that

$$(l^2+m^2+n^2+p^2+q^2+r^2)\xi+2(lr-mq+np)\eta \\ =(lr-mq+np)(\sigma_{11}+\sigma_{22}+\sigma_{33}+\sigma_{44})\,;$$

hence, by virtue of conditions (9) and (10), $\xi=0$.

Next form the sum of the products obtained by multiplying each equation of group (22) by the respective coefficient of η to find, by referring to (9), (19), and (21), that $\eta=\theta$. Hence equations (22) reduce to

$$\left.\begin{array}{ll} B_1-l\theta=0, & B_4-p\theta=0, \\ B_2-m\theta=0, & B_5-q\theta=0, \\ B_3-n\theta=0, & B_6-r\theta=0. \end{array}\right\} \quad . \quad . \quad . \quad (23)$$

Equations (23) are homogeneous and linear in the six direction-ratios l, m, n, p, q, r, so that a necessary and sufficient condition for a non-trivial solution is

$$\begin{vmatrix} \sigma_{11}+\sigma_{22}-\theta, & \sigma_{23}, & \sigma_{24}, & -\sigma_{13}, & -\sigma_{14}, & 0 \\ \sigma_{23}, & \sigma_{11}+\sigma_{33}-\theta, & \sigma_{34}, & \sigma_{12}, & 0, & -\sigma_{14} \\ \sigma_{24}, & \sigma_{34}, & \sigma_{11}+\sigma_{44}-\theta, & 0, & \sigma_{12}, & \sigma_{13} \\ -\sigma_{13}, & \sigma_{12}, & 0, & \sigma_{22}+\sigma_{33}-\theta, & \sigma_{34}, & -\sigma_{24} \\ -\sigma_{14}, & 0, & \sigma_{12}, & \sigma_{34}, & \sigma_{22}+\sigma_{44}-\theta, & \sigma_{23} \\ 0, & -\sigma_{14}, & \sigma_{13}, & -\sigma_{24}, & \sigma_{23}, & \sigma_{33}+\sigma_{44}-\theta \end{vmatrix} =0.$$

When expanded condition (24) would be a complete equation of the sixth degree in θ. The solution of this equation, especially in numerical cases, is very greatly facilitated by the remarkable property that a certain linear transformation removes all the terms of odd degree and thus reduces the solution to that of an equation of the third degree. The way in which this reduction may be effected will now be explained.

(*c*) Let τ denote the mean value of all the trinomial elements constituting the principal diagonal of the determinant in equation (24), that is:

$$\tau\equiv 1/2(\sigma_{11}+\sigma_{22}+\sigma_{33}+\sigma_{44})-\theta. \quad . \quad . \quad . \quad (25)$$

Also let

$$\left.\begin{array}{l} s_1\equiv 1/2(\sigma_{11}+\sigma_{22}-\sigma_{33}-\sigma_{44}), \\ s_2\equiv 1/2(\sigma_{11}-\sigma_{22}+\sigma_{33}-\sigma_{44}), \\ s_3\equiv 1/2(\sigma_{11}-\sigma_{22}-\sigma_{33}+\sigma_{44}), \end{array}\right\} \quad . \quad . \quad . \quad . \quad (26)$$

Substitution of expressions (25) and (26) in the determinant of (24) gives

$$\left.\begin{array}{cccccc}
a \quad a', & b \quad b', & c \quad c', & d \quad d', & e \quad e', & f \quad f' \\
s_1+\tau, & \sigma_{23}, & \sigma_{24}, & -\sigma_{13}, & -\sigma_{14}, & 0 \\
\sigma_{23}, & s_2+\tau, & \sigma_{34}, & \sigma_{12}, & 0, & -\sigma_{14} \\
\sigma_{24}, & \sigma_{34}, & s_3+\tau, & 0, & \sigma_{12}, & -\sigma_{13} \\
-\sigma_{13}, & \sigma_{12}, & 0, & -s_3+\tau, & \sigma_{34}, & \sigma_{24} \\
-\sigma_{14}, & 0, & \sigma_{12}, & \sigma_{34}, & -s_2+\tau, & \sigma_{23} \\
0, & -\sigma_{14} & \sigma_{13}, & -\sigma_{24}, & \sigma_{23}, & -s_1+\tau
\end{array}\right| \equiv U(\tau).$$

In the last determinant substitute $-\tau$ for τ and then multiply the second and fifth rows and the first, third, fourth, and sixth columns by -1 to find that $U(-\tau)=U(\tau)$. Therefore $U(\tau)$ is an even function of τ, that is, a function of τ^2, and $U(\tau)=0$ may be written as

$$\tau^6+a_2\tau^4+a_4\tau^2+a_6=0 \quad . \quad . \quad . \quad . \qquad (27)$$

Formulæ for the coefficients a_2, a_4, and a_6 may be obtained in the following manner:—Imagine five zero constituents written in each of the columns of the above determinant headed a', b', c', d', e', and f'. Thus the columns of $U(\tau)$ are to be considered as composed of binomial constituents, the second term in each sum being either τ or zero. $U(\tau)$ may now be developed as the sum of sixty-four (2^6) determinants each of which comprises six of its monomial columns.

The fifteen determinants involving τ^4 may be indicated by the headings of the monomial columns in $U(\tau)$ as $abc'd'e'f'$, $ab'cd'e'f'$, $ab'c'de'f'$, $ab'c'd'ef'$, $ab'c'd'e'f$, $a'bcd'e'f'$, $a'bc'de'f'$, $a'bc'd'ef'$, $a'bc'd'e'f$, $a'b'cde'f'$, $a'b'cd'ef'$, $a'b'cd'e'f$, $a'b'c'def'$, $a'b'c'de'f$, $a'b'c'd'ef$. The evaluation of these determinants leads to

$$-a_2 = s_1^2+s_2^2+s_3^2+2(\sigma_{12}^2+\sigma_{13}^2+\sigma_{14}^2 \\ +\sigma_{23}^2+\sigma_{24}^2+\sigma_{34}^2). \quad . \qquad (28)$$

Hence, a_2 is essentially negative for real values of the coordinates of the given points.

In the same notation, the fifteen determinants involving τ^2 are $abcde'f'$, $abcd'ef'$, $abcd'e'f$, $abc'def'$, $abc'de'f$, $abc'd'ef$, $ab'cdef'$, $ab'cde'f$, $ab'cd'ef$, $ab'c'def$, $a'bcdef'$, $a'bcde'f$, $a'bcd'ef$, $a'bc'def$, $a'b'cdef$. From these it will be found that

$$a_4=(s_1s_2+\sigma_{14}^2-\sigma_{23}^2)^2+(s_1s_3+\sigma_{13}^2-\sigma_{24}^2)^2+(s_2s_3+\sigma_{12}^2-\sigma_{34}^2)^2 \\ +2(\sigma_{12}s_1+\sigma_{13}\sigma_{23}+\sigma_{14}\sigma_{24})^2+2(-\sigma_{34}s_1+\sigma_{13}\sigma_{14}+\sigma_{23}\sigma_{24})^2 \\ +2(\sigma_{13}s_2+\sigma_{12}\sigma_{23}+\sigma_{14}\sigma_{34})^2+2(-\sigma_{24}s_2+\sigma_{12}\sigma_{14}+\sigma_{23}\sigma_{34})^2 \\ +2(\sigma_{14}s_3+\sigma_{12}\sigma_{24}+\sigma_{13}\sigma_{34})^2+2(-\sigma_{23}s_3+\sigma_{12}\sigma_{13}+\sigma_{24}\sigma_{34})^2. \\ . \quad . \quad . \qquad (29)$$

Accordingly, a_4 is essentially positive for real values of the coordinates. On changing signs throughout the fifth row and the fifth column of $U(0)$ it becomes evident that the determinant is skew-symmetrical with respect to the negative diagonal. Hence a_6 must equal the negative of a perfect square; in fact,

$$a_6 = -[s_1s_2s_3 + (\sigma_{12}^2 - \sigma_{34}^2)s_1 + (\sigma_{13}^2 - \sigma_{24}^2)s_2 + (\sigma_{14}^2 - \sigma_{23}^2)s_3 + 2(\sigma_{12}\sigma_{13}\sigma_{23} + \sigma_{12}\sigma_{14}\sigma_{24} + \sigma_{13}\sigma_{14}\sigma_{34} + \sigma_{23}\sigma_{24}\sigma_{34})]^2. \quad (30)$$

The conditions under which the preceding analysis "fails" will not be investigated in this paper, because they depend upon very special distributions of the given points. Such cases afford no difficulty, for they mean simply that no minimum plane exists. Analogous conditions present themselves in three-space, for illustration, when the associated ellipsoid having three unequal axes degenerates into a spheroid or a sphere. Cases of this kind would not arise when the residuals are small enough to justify employing the Method of Least Squares for the determination of the parameters in the equations of the plane.

(*d*) As a concrete illustration of the foregoing theory, the following data may be used:—(0, 0, 0, 0), (1, 1, 1, −1), (2, 1, −1, 0), (1, −1, 1, 2), (1, 2, −1, −1), (2, −1, 1, −1), (0, −1, −1, 1). These seven points have been chosen so that no five of them lie in the same hyperplane. It follows that $\sigma_{11}=28$, $\sigma_{22}=62$, $\sigma_{33}=42$, $\sigma_{44}=56$, $\sigma_{12}=7$, $\sigma_{13}=7$, $\sigma_{14}=-14$, $\sigma_{23}=-21$, $\sigma_{24}=-35$, $\sigma_{34}=0$, $s_1=-4$, $s_2=-24$, $s_3=-10$, $\kappa=7$, $\bar{w}=1$, $\bar{x}=1/7$, $\bar{y}=\bar{z}=0$. Substituting in formulas (28), (29), and (30), it will be found that

$$(\tau^2)^3 - 4612(\tau^2)^2 + 4438236(\tau^2)^1 - 1177862400 = 0.$$

Approximate values of the roots of this cubic are

$$\tau_1^2 = 3412{\cdot}5946, \quad \therefore \tau_1 = \pm 58{\cdot}4174,$$
$$\tau_2^2 = 720{\cdot}0844, \quad \therefore \tau_2 = \pm 26{\cdot}8344,$$
$$\tau_3^2 = 479{\cdot}3210, \quad \therefore \tau_3 = \pm 21{\cdot}8934,$$

with $\theta = 94 - \tau$. The minimum value of θ obviously corresponds to the positive value of τ_1. Substitution of this value of θ in equations (23) led to the following five ratios:

$$\frac{m}{l} = 0{\cdot}7826, \quad \frac{n}{l} = 0{\cdot}8641, \quad \frac{p}{l} = 0{\cdot}3213, \quad \frac{q}{l} = -0{\cdot}3922,$$
$$\frac{r}{l} = -0{\cdot}5845.$$

Relation (9) now furnishes

$$l = +0{\cdot}58145, \qquad p = +0{\cdot}1868,$$
$$m = +0{\cdot}4550, \qquad q = -0{\cdot}2280,$$
$$n = +0{\cdot}5024, \qquad r = -0{\cdot}3399.$$

The following approximate values for the perpendicular distances between the seven given points and the minimum plane were computed by means of formula (12):—

$$\Delta_1 = 0{\cdot}8932, \qquad \Delta_4 = 0{\cdot}9638,$$
$$\Delta_2 = 0{\cdot}8333, \qquad \Delta_5 = 0{\cdot}1540,$$
$$\Delta_3 = 1{\cdot}1785, \qquad \Delta_6 = 0{\cdot}8505,$$
$$\Delta_7 = 0{\cdot}7254.$$

Incidentally the coordinates of the foot of the perpendicular dropped from the origin upon the minimum plane were calculated by the aid of equations (15) to be approximately $w = +0{\cdot}79335$, $x = +0{\cdot}0311$, $y = -0{\cdot}2305$, $z = +0{\cdot}3381$. Finally, the equations of the minimum plane may be taken as

$$\left.\begin{array}{l} 4550w + 1868x + 3399z - 4817 = 0 \\ 5815x + 4550y + 5024z - 831 = 0 \end{array}\right\}.$$

In conclusion, the writer desires to call attention to an interesting by-product of the preceding analysis. Since $\theta = \kappa\phi$ and ϕ denotes the sum of the squares of the perpendicular distances from the κ points of the given system to the plane, it follows that if all these points were to become co-planar then θ would equal zero and, conversely, if all the coordinates are real and $\theta = 0$ all the points will lie in a single plane. [If the points become collinear they may still be considered co-planar, although the plane may be indeterminate.] Therefore a necessary and sufficient condition that any number of real points shall lie in a plane in four-space is the vanishing of the determinant obtained by putting $\theta = 0$ in the left-hand side of equation (24). [For sake of elegance, change signs throughout the fifth row and the fifth column.]

Obviously a complete set of criteria for the order of the linearity of a system of points in four-space is afforded by the constant terms in the "θ-equations" for the hyperplane, the plane (*vide supra*), and the straight line. The author is now engaged in the complete generalization of the preceding problem to a k-flat in an n-flat, $k < n$.

Yale University,
November 1924.

CXXVIII. *Applications of the Correspondence Principle to the Theory of Line-intensities in Band-spectra.* By R. H. FOWLER [*].

§ 1. *INTRODUCTION.*—The object of this paper is to present the theoretical laws governing the intensities of the lines in any single band, so far as these can yet be based on applications of the Correspondence Principle. It will be found that certain quantitative deductions can be drawn with considerable certainty. The work consists in a natural extension to these spectra of the ideas of Heisenberg [†], which have proved so successful in interpreting the quantitative intensity theory of atomic spectra of "the first rank" [‡]. The resulting formulæ are compared with the existing experimental material, and appear to be in satisfactory agreement, but the material for comparison is hardly yet quantitatively reliable. Certain subsidiary discrepancies remain which may be highly significant.

By way of introduction it is convenient to summarize here those applications of the Correspondence Principle which have special reference to band-spectra, and to stress their typical resemblances. It is in this way perhaps easier to see that they form a corporate whole. In the first instance, as is well known, the Correspondence Principle asserts, on account of the asymptotic equality of frequencies for large quantum numbers, a similar asymptotic equality between the intensities and polarizations of the light radiated by atoms (or molecules) according to the classical and the quantum theories. This assertion is unambiguous and quantitative. Outside the region of large quantum numbers the switches of the quantum theory can still be unambiguously related to terms in the Fourier development of the electrical moment of the atom (or molecule), and the frequencies of the light emitted according to the quantum theory can still be quantitatively described in terms of the mechanical motions. It is, however, only possible in general to postulate a qualitative correspondence between the probabilities of quantum switches and the Fourier coefficients, and so only a qualitative connexion between intensities and polarizations in the two theories. The lack of any more quantitative general correspondence is natural enough, and in fact essential, since the response of atoms to radiation, whether or not described in terms of virtual oscillators, can only be connected in a symbolical way with the mechanical motions in the stationary states.

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[*] Communicated by the Author.

[†] Heisenberg, *Zeit. für Phys.* xxxi. p. 617 (1925).

[‡] Landé, "*erster stufe.*"

One significant exception has been recognized from the first *—that the complete absence of particular terms of the Fourier series may be taken to imply that the corresponding switches of the quantum theory never occur with emission or absorption of radiation (or only with certain polarizations). Their probabilities (or some of their component probabilities) are exactly zero. Such an application—valid for all quantum numbers and not merely asymptotically—will be described as *refined*. This first refined application is of course of particular importance in band-spectra, for progress in their theory would have been entirely impossible without the resulting selection rule $\Delta m = \pm 1$ or $\Delta m = 0, \pm 1$ for changes of the rotational quantum number m. The argument in this refined application may be stated thus:—On the classical theory the atom would *never* emit or absorb radiation of such and such frequencies. It must therefore be presumed that the corresponding quantum switches will *never* occur.

Quite recently it has been shown, especially by Heisenberg, that other such refined applications can be made. The simplest and most certain of these is the one required in the present paper. On the classical theory an atom, of the usual lightly coupled core-series-electron type, will emit radiation of a *total* amount which does *not* depend on the angle between the plane of the orbit of the series electron and the axis of resultant angular momentum. [The intensities of the various components in the light will of course depend notably on this angle.] It must therefore be expected that the corresponding *total* emission in the quantum theory will *not* depend on this angle—*i. e.* not depend on the third quantum number j. [The independence in this case is not absolutely exact on the classical theory; it would be in default by quantities of the extremely small order ω_j/ω_n compared with 1, where ω_j is the precessional frequency of the orbital plane, and ω_n the frequency of the electron in its quasi-Keplerian orbit, but one must believe that this is trivial.] This refined application leads at once, as Heisenberg has shown, to the exact Ornstein–Burger–Dorgelo † summation rules. In the hands of Kronig ‡ (in conjunction with a normal asymptotic application) it has yielded complete exact rules for the intensity ratios of all the lines in any multiplet [other than intercombinations] in any spectrum of the first rank, and of all their Zeeman components in weak and strong fields. Theory and experiment appear to be in full agreement, though a wider range of experimental material is required *.

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* Bohr, *Danske Vid. Selsk. Skrifter*, iv. p. 16 (1918).

† *Zeit. für Phys.* xxiii. p. 258; xxiv. p. 24; xxviii. p. 135; xxix. p. 241 (1924).

‡ Kronig, *Zeit. für Phys.* xxxi. p. 885 (1925).

The common idea underlying these refined applications is that when classical theory demands unambiguously a certain null effect, then the quantum theory also must provide for a similar null effect; whereas when there is a certain positive effect in the classical theory there will be some positive effect in the quantum theory which need only (and generally will only) be asymptotically the same for large quantum numbers. It is evident that a similar refined application can be made to the theory of line-intensities in band-spectra—put simply, that the Ornstein–Burger–Dorgelo summation rules must hold for the lines of a single band, other than a pure rotation band, just as for the lines of a single multiplet. The rest of this paper will be concerned with the formal development of these rules in various cases and their comparison with observations. The rules themselves are probably more reliable than our theoretical knowledge of the weights of the various molecular states, at least in certain cases, and a quantitative study of line intensities in a band may well throw light on these and other points in molecular structure.

With regard to the experimental facts, the general symmetry of the observed intensities of the lines in the positive and negative branches of a band is well known. It is found both in infra-red absorption bands (*e. g.* HCl) and in the more complicated bands in the visible region (*e. g.* "Cyanogen" bands) †. The intensities of the lines increase regularly from the beginning of the branches, attain a maximum intensity and then fade away. The position of the maximum on the branch exhibits a well-recognized dependence on temperature, which has even been tentatively employed as an index of the temperature of stellar reversing layers*. The theory of these intensities has recently been taken up by Kemble†, who has pointed out the apparent difficulty that the first pair of lines in the positive and negative branches of a band are now normally classified as due to the (absorption) switches $\frac{1}{2}\rightarrow\frac{3}{2}$ and $\frac{3}{2}\rightarrow\frac{1}{2}$ respectively in rotational quantum number‡. It is not immediately obvious that there is any theoretical reason, *purely on grounds of symmetry*, for the equality in strength of these two lines. Kemble experiments with various solutions, and decides in favour of one which is in substantial agreement with experiment, and is based on a tentative application of the Correspondence Principle, in essentials the same as that established by Heisenberg and described above. It will be one object of this paper to bring Kemble's suggestion into its proper relationship with other refined applications of the Correspondence Principle, and to show that unambiguous results can be reached practically without calculation.

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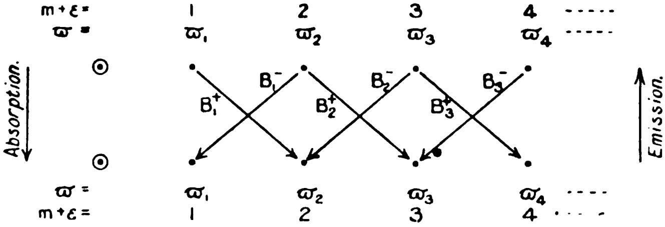
* Besides the refined applications relevant here, two other such applications, equally interesting, have been proposed by Heisenberg (*loc. cit.*), one to the problem of spectroscopic continuity, and the other to the state of polarization of scattered and resonance radiation, and the experiments of Wood and Ellett. These can only be mentioned in passing, but they appear strongly to confirm the validity of the whole idea on which refined applications are based.

† Sommerfeld, *Atombau u. Spektrallinien*, ed. 4, pp. 711, 722-4.

§ 2. *Band structure.*—An adequate model for the discussion of the structure of a simple band or set of bands is the oscillating-rotating dipole. It follows at once, by the old refined application of the Correspondence Principle, that the selection rule for m is $\Delta m = \pm 1$. A null branch, $\Delta m = 0$, can only occur if the molecule has an electric moment along its axis of rotation. In no circumstances can this model or the generalizations of Kramers and Pauli § lead to any selection rule more general than $\Delta m = 0, \pm 1$. For any model the structure of a simple band with no zero branch is now usually represented formally as under. The arrows represent the various absorption switches in m, and the $B_n{}^{\pm}$ against them the relative molecular absorption probabilities ||.



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* Birge, Astrophys. J. lv. p. 273 (1922).

† Kemble, Phys. Rev. xxv p. 1 (1925).

‡ Sommerfeld, *loc. cit.* p. 712.

§ Kramers & Pauli, *Zeit. für Phys.* xiii. p. 351 (1923).

|| Different suffix letters, n and m, will be deliberately used for lines and states. This may help to avoid confusion.

It is assumed that the initial and final states can be paired in such a way that for any pair both m and ϖ are equal. This follows for any simple model from the principles of the quantum theory, and may be true in general. On any simple theory we must also expect that

$$\varpi_m \propto m+\epsilon+\alpha \quad (\varpi_1 \propto 1+\alpha, \text{ etc.}),$$

where α is constant. [For simple dipoles α is probably either $-\frac{1}{2}$ or 0. It can be left indefinite in the following arguments.] The relative numbers of molecules in the various initial states in statistical equilibrium will be proportional to

$$\varpi_m e^{-\delta m^2/T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where δ is (roughly) constant and T is the absolute temperature. [This formula will be slightly modified on the theory of Kramers and Pauli.]

§ 3. *The Summation Rules, and the relative Absorption Coefficients.*—To make the necessary further refined application of the Correspondence Principle, we have only to observe that on the classical theory the total reaction of the oscillating-vibrating dipole (or similar model) to radiation must to a close approximation be independent of the rotational quantum number m. This will be true so long as the frequency of rotation σ is very small compared with the vibration frequency ω, and so long as the centrifugal force does not appreciably affect the vibrational motion, which is secured by the same condition. The deviations from equality must be expected to be of the order σ/ω compared with 1, so that the equality will hold so long as m is not too large. It follows at once, by a refined application, that, so long as we may ignore differences of wave-length among the switches,

$$B_1^+ = B_1^- + B_2^+ = B_2^- + B_3^+ = \ldots\ldots \quad . \quad . \quad (2)$$

A second set of equations is obtained by the application of the same argument to the process of emission. Denote the corresponding molecular emission coefficients by $A_n^{\pm}$. Then

$$A_1^- = A_1^+ + A_2^- = A_2^+ + A_3^- = \ldots\ldots \quad . \quad . \quad (3)$$

The $A_n^{\pm}$ and $B_n^{\pm}$ are (or are proportional to) Einstein's probability coefficients, and according to his well-known analysis satisfy the equations

$$\frac{8\pi h\nu^3}{c^3}\varpi_n B_n^+ = \varpi_{n+1} A_n^+, \quad \frac{8\pi h\nu^3}{c^3}\varpi_{n+1} B_n^- = \varpi_n A_n^- \quad . \quad (4)$$

Again ignoring differences of wave-length, equation (4) indicates that for each switch

$$\varpi_n B_n^+ / \varpi_{n+1} A_n^+ \quad \text{or} \quad \varpi_{n+1} B_n^- / \varpi_n A_n^-$$

is constant. To put these equations in symmetrical form, let us write

$$\varpi_n B_n^+ = b_n^+, \quad \varpi_{n+1} B_n^- = b_n^- . \quad . \quad . \quad . \quad (5)$$

The $b_n^\pm$ then denote the product of the molecular absorption probabilities in any state by the weight of that state, and in terms of the $b_n^\pm$ the equations (2) and (3) can be written *

$$\frac{b_1^+}{\varpi_1} = \frac{b_1^- + b_2^+}{\varpi_2} = \frac{b_2^- + b_3^+}{\varpi_3} = \ldots\ldots = X, \quad . \quad (6)$$

$$\frac{b_1^-}{\varpi_1} = \frac{b_1^+ + b_2^-}{\varpi_2} = \frac{b_2^+ + b_3^-}{\varpi_3} = \ldots\ldots = Y \quad . \quad . \quad (7)$$

Relative absorption coefficients for the different lines are given by the ratios of the $b_n^\pm$ multiplied by the exponential factors only from (1).

Equations (6) and (7) suffice to determine all the $b_n^\pm$ in terms of X and Y, but do not immediately determine the ratio X/Y itself. If we solve (6) and (7) for $b_n^\pm$ we find

$$\left.\begin{aligned} b_n^+ &= (\varpi_n + \varpi_{n-2} + \ldots)X - (\varpi_{n-1} + \varpi_{n-3} + \ldots)Y \\ b_n^- &= (\varpi_n + \varpi_{n-2} + \ldots)Y - (\varpi_{n-1} + \varpi_{n-3} + \ldots)X \end{aligned}\right\} . \quad (8)$$

Hence if any pair of b_n are equal, then X=Y and all pairs of b_n must be equal. That X and Y must in general be equal can be inferred in several ways, of which the most fundamental seems to rest on a further refined application of the Correspondence Principle. We have already seen in this way that the total radiative activity of any state of the molecule must not depend on the rotation. Suppose the molecule can be reduced to rest and possesses two vibrational states. There will be certain probabilities for the switches to and from these states, connected by Einstein's equations. Its total radiative activity must, however, be the same as if it were rotating, and the same relation must therefore hold between the probability coefficients, although in the rotating states these are no longer paired together. If we form Einstein's equation for the non-rotating states in the notation of equations (6) and (7), we find $b' = b''$. By the refined

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* These arguments form of course the general basis for the interpretation of the rules of Ornstein, Burger, and Dorgelo. They have been repeated here in detail, particularly to stress the independence of (6) and (7) of temperature, which is far more important here than in the theory of *atomic* spectra.

application of the Correspondence Principle here in question, we must have $b' = b_1^+$ and $b'' = b_1^-$, so that $b_1^+ = b_1^-$, and therefore $X = Y$ etc., as above.

This argument is somewhat unusual, and it is comforting to confirm it by other arguments, formally simpler but less direct. The asymptotic equality of pairs of b_n in the limit of large n can be inferred from an ordinary application of the Correspondence Principle. This implies $X = Y$. Again, using $\varpi_m = m + \alpha$, we find

$$\left.\begin{aligned} b_{2n}^+ &= n(n+\alpha)(X-Y) + nX, \\ b_{2n}^- &= n(n+\alpha)(Y-X) + nY. \end{aligned}\right\} \quad . \quad . \quad . \quad (9)$$

There is therefore an algebraic necessity for $X = Y$, for otherwise, for sufficiently large n, we arrive at impossible negative intensities. We conclude that

$$\left.\begin{aligned} b_{2n}^+ = b_{2n}^- &= nX &&= \tfrac{1}{2}(\varpi_{2n} - \alpha)X, \\ b_{2n-1}^+ = b_{2n-1}^- &= (n+\alpha)X &&= \tfrac{1}{2}(\varpi_{2n-1} + \alpha + 1)X. \end{aligned}\right\} (\varpi_n = n + \alpha). \quad . \quad . \quad . \quad (10)$$

The actual relative absorption coefficients $\alpha_n^\pm$ will be given by multiplying the $b_n^\pm$ of (10) by the temperature factor. Thus

$$\left.\begin{aligned} \alpha_{2n}^+ &= nXe^{-\delta(2n-2\epsilon)^2 T}, & \alpha_{2n-1}^+ &= (n+\alpha)Xe^{-\delta(2n-1-2\epsilon)^2 T}, \\ \alpha_{2n}^- &= nXe^{-\delta(2n+1-2\epsilon)^2 T}, & \alpha_{2n-1}^- &= (n+\alpha)Xe^{-\delta(2n-2\epsilon)^2 T}. \end{aligned}\right\} (11)$$

§ 4. *Infra-red bands, in particular of HCl.*—If $\alpha = -\frac{1}{2}$, and variations of wave-length are ignored (the theory can hardly be extended so far as to make their inclusion significant), formula (10) gives $b_n^\pm$ a sequence of values proportional to 2, 4, 6, 8, ... If $\alpha = 0$ the sequence is 4, 4, 8, 8, 12, 12, ... By an argument based as stated on the same fundamental idea, but differing in detailed development *, Kemble arrives at a formula [(21) of his paper] for the absorption coefficients, equivalent to (10) and (11) here if the $b_n^\pm$ have the sequence of values 3, 5, 7, 9, ... He has further shown that his formula is in substantial agreement with the observations on the main band of HCl at 3·5 μ. The observations could hardly distinguish between Kemble's sequence of $b_n^\pm$ and the sequence 2, 4, 6, 8, ... or perhaps even 4, 4, 8, 8, 12, 12, ... The present theory may therefore be taken to be equally in agreement with experiment. There are no outstanding discrepancies, in particular none for the first pair of lines, and the positions of the lines of maximum intensity are properly predicted not only for this band but also for the overtone band at 1·7 μ and for the bands of HF and HBr. It will be observed that the predicted line intensities are slightly asymmetrical owing to the temperature factor; in cases of absorption such as these $\alpha_n^+ > \alpha_n^-$. *The absorption line of shorter wave-length should be stronger, by a factor depending on the temperature, than the corresponding line of longer wave-length in the other branch.* In the usual terminology, in absorption the positive branch should be stronger than the negative.

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* I do not think that Kemble's development can be maintained against the more direct development of this paper.

It must not be forgotten, a point brought out by Kemble, that the observations give total percentage absorptions by a given length of absorbing gas, so that except when these percentages are less than 20 or at most 30, they cannot be directly compared with atomic absorption coefficients. A detailed study of the temperature variation of the relative intensities of the HCl and other absorption bands, especially when the total absorption is never allowed to get too high, might provide information of interest. It hardly seems possible in view of the success of similar refined applications of the Correspondence Principle in other fields to doubt the correctness of equations (11) for not too large n if the assumed structure of § 2 is correct.

When we attempt to compare the observations on other infra-red bands * with equations (11), especially in respect of the predicted asymmetry, we meet with grave anomalies. I. In the overtone band of HCl at 1·75 μ, the total absorption lies between 20 per cent. and 30 per cent. and favours a comparison with theory. The first pair of lines appear equal. In all other pairs except the 3rd, the line of shorter wave-length (the positive branch) is (apparently) the stronger, according to theory. The 3rd pair, of maximum intensity, is exceptional. II. In the band of HF at 2·5 μ again the first pair are equal and the other pairs except the 2nd (maximum pair) stronger in the positive branch. The absorptions here, however, are rather high, running up to 90 per cent. III. In the band of HBr at 3·9 μ the lines in the negative branch are uniformly stronger! If attention is paid only to the single maximum line, then in all these cases, including perhaps even the main band of HCl, one is tempted to say that the *negative* branch is the stronger, but I believe this generalization to be quite unwarranted by the observations recorded. There is, however, clearly occasion here for further interesting experimental work for comparison with theory.

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* Imes, Astrophys. J. l. p. 251 (1919).

Quantitative comparisons beyond those worked out by Kemble are hardly likely to be of value, except perhaps for the small absorptions in the overtone band of HCl. It follows at once from equations (11) that

$$\frac{\alpha_n{}^+}{\alpha_n{}^-}=e^{\delta(2n-2\epsilon+1)/T}. \quad . \quad . \quad . \quad . \quad (11\cdot1)$$

[For simplicity the most probable case $\epsilon=\frac{1}{2}$, $\alpha=-\frac{1}{2}$ will alone be considered.] It follows further that if $n^\times$ is the value of n (not necessarily integral) for which the positive branch attains its maximum intensity, then

$$2\delta(n^\times)^2/T=1. \quad . \quad . \quad . \quad . \quad . \quad (11\cdot2)$$

Therefore

$$\frac{\alpha_n{}^+}{\alpha_n{}^-}=e^{n/(n^\times)^2}. \quad . \quad . \quad . \quad . \quad . \quad (11\cdot3)$$

For HCl as recorded by Imes, $n^\times=3$. The computed and observed intensity ratios are as follows:—

n.	Ratios.	
	Obs.	Calc.
1	1·0	1·1
2	1·15	1·2
3	0·95	1·4
4	1·3	1·5
5	1·25	1·7
6	1·25	1·8

The entries for the observed ratios are very rough, being obtained merely by reading off *maximum ordinates*. The greatest absorption is only 36 per cent. In spite of the deviations, which are of a type which must contain large experimental errors, there is no reason to believe in any systematic deviation from the theory. At least the sometimes expressed opinion that the negative branch (of longer wave-length) is the stronger is not borne out by these observations.

§ 5. *Visible bands, and bands with zero branches.*—Bands in the visible and ultra-violet regions are in general studied in emission, and in general the constant δ in equation (1) is very small. The temperature factor can only be sensible for small m if the molecule contains at most one atom heavier than He. Moreover, the effective temperature of the emitting material will normally be controlled by the mean energy of the bombarding electrons and so in general be very high. The intensities of the earlier emission lines should therefore be effectively proportional to $b_n{}^{\pm}$. The intensities will be cut down to zero by the temperature factors later in the sequences. We should therefore get full symmetry in the *initial* intensities of the positive and negative branches of a band with no zero branch, which at first increase steadily along the branches according to the law (10). The general features of this intensity distribution are precisely those observed, but it will be interesting to know in detail whether the law (10), and if so for what value of α, is quantitatively observed in the early lines. If $\alpha=-\frac{1}{2}$ the early intensities will be in arithmetical progression. If $\alpha=0$ they will be equal in pairs, and the pairs will be in such a progression. Such evidence as is available is discussed in § 6.

We can write down in a similar way some of these equations for the intensities in the more usual type of bands which contain zero branches, corresponding to $\Delta m=0$. Let $b_n{}^0$ have the same meaning for the zero branch that $b_n{}^{\pm}$ have for the other branches. Then

$$\left.\begin{aligned}\frac{b_1{}^0+b_1{}^+}{\varpi_1}=\frac{b_1{}^-+b_2{}^0+b_2{}^+}{\varpi_2}=\frac{b_2{}^-+b_3{}^0+b_3{}^+}{\varpi_3}=\ldots\ldots=\mathrm{X},\\ \frac{b_1{}^-+b_1{}^0}{\varpi_1}=\frac{b_2{}^-+b_2{}^0+b_1{}^+}{\varpi_2}=\frac{b_3{}^-+b_3{}^2+b_2{}^+}{\varpi_3}=\ldots\ldots=\mathrm{Y}.\end{aligned}\right\}. \quad (12)$$

From the symmetry of these equations it is at once clear that if $b_n{}^+=b_n{}^-$ for any value of n, then $\mathrm{X}=\mathrm{Y}$ and $b_n{}^+=b_n{}^-$ for all values of n. We can again conclude by a refined application of the Correspondence Principle to a comparison of the rotating molecule with the molecule at rest that $b_1{}^+=b_1{}^-$ and therefore that $\mathrm{X}=\mathrm{Y}$ etc., as before. The temperature factors in such bands are usually unimportant for early n's. The theory thus still predicts the observed symmetry, and in addition the relations

$$\frac{b_1{}^0+b_1{}^+}{\varpi_1}=\frac{b_2{}^0+b_2{}^++b_1{}^-}{\varpi_2}=\frac{b_3{}^0+b_3{}^++b_2{}^-}{\varpi_3}=\ldots\ldots=\mathrm{X} \quad (13)$$

between the intensities of the zero and the positive (or negative) branch.

It is clear that the equations above give the maximum information possible without more detailed molecular models.

The pictorial value of these is still somewhat uncertain, but perhaps the use of a particular model, and an attempt to proceed beyond equations (13), similar to Kronig's work, may not be entirely unfruitful. Let us consider the following model:—a quasi-rigid diatomic molecule, moving like a spinning-top, with an electronic moment of momentum $jh/2\pi$ about the line of nuclei, in steady precessional motion about its invariable axis with a total moment of momentum $mh/2\pi$ $(m > j)$. The rigid body contains an electric moment (expressed in multiple Fourier Series) with components along the line of nuclei and along axes at right angles. Let the electric moment, when the line of nuclei of the molecule is at rest, have components X, Y, Z along axes fixed in space given by

$$X = \tfrac{1}{2}\Sigma_\tau X_\tau e^{2\pi i(\omega\tau)t}, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

etc., where X_τ is a complex number and $X_{-\tau}$ its conjugate. The axis Z is the line of nuclei. Now suppose that the invariable axis R lies in the plane of Z and X and makes an angle θ with OZ, necessarily such that

$$\cos\theta = j/m. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Take a set of three instantaneous axes P, Q, R of which Q coincides with Y. Then the amplitudes of the electric moments along these axes are

$$\begin{aligned} R_\tau &= Z_\tau \cos\theta + X_\tau \sin\theta, \\ Q_\tau &= Y_\tau, \\ P_\tau &= -Z_\tau \sin\theta + X_\tau \cos\theta. \end{aligned}$$

These axes are, however, rotating about OR with frequency σ. The electric moments $P_\tau{}^0$, $Q_\tau{}^0$, $R_\tau{}^0$, referred to axes fixed in space, momentarily coinciding with P, Q, R, are therefore

$$\begin{aligned} R_\tau{}^0 &= Z_\tau \cos\theta + X_\tau \sin\theta, \\ P_\tau{}^0 + iQ_\tau{}^0 &= (P_\tau + iQ_\tau)e^{-2\pi i\sigma t} \\ &= \{(-Z_\tau \sin\theta + X_\tau \cos\theta) + iY_\tau\}e^{-2\pi i\sigma t}. \end{aligned}$$

It follows that the squares of the amplitudes of the components of frequencies $(\omega\tau) \pm \sigma$ in both P and Q are respectively

$$\tfrac{1}{4}\{(-Z_\tau \sin\theta + X_\tau \cos\theta) \mp iY_\tau\} \\ \{-Z_{-\tau} \sin\theta + X_{-\tau} \cos\theta) \pm iY_{-\tau}\} \quad . \quad . \quad (16)$$

In evaluating this expression we must, however, remember that the invariable axis R may have any position whatever in the XY plane of the molecule and that the square of the amplitude above must be averaged over all such positions to give the mean square amplitude for a number of atoms. This means that we must replace X_τ and Y_τ by zero, $X_\tau X_{-\tau}$ and $Y_\tau Y_{-\tau}$ by $\frac{1}{2}(X_\tau X_{-\tau}+Y_\tau Y_{-\tau})$, while $X_{-\tau}Y_\tau - X_\tau Y_{-\tau}$ is invariant.

The mean value of the expression (16) is therefore

$$\tfrac{1}{4}\{Z_\tau Z_{-\tau}\sin^2\theta+\tfrac{1}{2}(X_\tau X_{-\tau}+Y_\tau Y_{-\tau})(1+\cos^2\theta) \mp i(X_{-\tau}Y_\tau - X_\tau Y_{-\tau})\cos\theta\}. \quad (17)$$

The mean square amplitude of the corresponding term of frequency $(\omega\tau)$ in R is the mean value of

$$(Z_\tau\cos\theta+X_\tau\sin\theta)(Z_{-\tau}\cos\theta+X_{-\tau}\sin\theta),$$

or

$$Z_\tau Z_{-\tau}\cos^2\theta+\tfrac{1}{2}(X_\tau X_{-\tau}+Y_\tau Y_{-\tau})\sin^2\theta. \quad . \quad (18)$$

To the approximation which ignores the frequency differences between $(\omega\tau)\pm\sigma$ and $(\omega\tau)$, the rate of radiation of energy is proportional to the sum of the squared amplitudes, and is therefore independent, as it should be, of θ.

It is a deduction therefore from classical theory that the intensities in the positive, negative, and zero branches of a classical band should all be expressible in the form

$$Q(\cos\theta),$$

where Q is a quadratic. Since $\cos\theta=j/m$, we are therefore entitled (following Kronig) to assume that the molecular emission coefficients (Einstein's A's) can be expressed in the form

$$Q_1(m)/Q_2(m),$$

where Q_1 and Q_2 are both quadratic functions. We have, however, worked above in terms of b_n, where each b is proportional to the corresponding ϖA, ϖ being the weight of the state from which the emission switch A starts. Thus we are entitled to assert that, in the quantum theory, we shall find

$$\left.\begin{aligned} b_n{}^+ &= \varpi_{n+1}\frac{Q_1(n)}{Q_2(n)}, \\ b_n{}^- &= \varpi_n\frac{Q_1{}'(n)}{Q_2{}'(n)}, \\ b_n{}^0 &= \varpi_n\frac{Q_1{}''(n)}{Q_2{}''(n)}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

all the Q's being quadratics. Since we have already proved that $b_n^+ = b_n^-$, we must have

$$\varpi_{n+1}\frac{Q_1(n)}{Q_2(n)} \equiv \varpi_n \frac{Q_1'(n)}{Q_2'(n)} \qquad (\varpi_n = n+\alpha).$$

It follows that ϖ_n must be a factor of either Q_1 or Q_2' and similarly for ϖ_{n+1}; all possibilities reduce to two,

$$b_n^{\pm} = \varpi_{n+1}\varpi_n \frac{L(n)}{Q(n)} \text{ or } \frac{Q(n)}{L(n)}, \quad . \quad . \quad . \quad (20)$$

where $L(n)$ is a linear function. The form of b_n^0 must be left general, as in (19) above. We have to satisfy equations (13) with functions of the form (20). In the first case the form of $L(n)$ is determined by the initial condition that b_n^- must vanish for the first state ($b_0^- = 0$). We may suppose further that from the structure of the molecule and the Correspondence Principle we know the ratio b_n^0/b_n^+ (say $\kappa:\frac{1}{2}$) for large n. We can therefore assume

$$\left.\begin{aligned} b_n^{\pm} &= \frac{\frac{1}{2}(n+\alpha+1)(n+\alpha)n}{(1+\kappa)(n+A_1)(n+B_1)}X, \\ b_n^0 &= \frac{\kappa(n+\alpha)(n+C_2)(n+D_2)}{(1+\kappa)(n+A_2)(n+B_2)}X. \end{aligned}\right\} \quad . \quad . \quad . \quad (21)$$

There are then as many conditions to be satisfied as there are undetermined coefficients, and just *two* solutions of the equations (13) as an identity in n. This is easily verified. One of these is

$$b_n^{\pm} = \frac{\frac{1}{2}n}{1+\kappa}X, \quad b_n^0 = \left\{\frac{\kappa n + \frac{1}{2}}{1+\kappa} + \alpha\right\} X \quad . \quad . \quad (22)$$

The other coincides with (22) when $\alpha = -\frac{1}{2}$. When $\alpha \neq -\frac{1}{2}$ neither solution is physically significant, since it is easily found that b_n^0 does not vanish with κ. That it must so vanish follows at once from the usual refined application of the Correspondence Principle. This however is to be expected, since when $\alpha \neq -\frac{1}{2}$ our original solution for no zero branch cannot be put into the form (19), for odd and even b's must be represented by different formulæ. The second alternative in (20) requires us to assume that

$$\left.\begin{aligned} b_n^{\pm} &= \frac{\frac{1}{2}n(n+A_1)}{(1+\kappa)(n+C_1)}X, \\ b_n^0 &= \frac{\kappa(n+\alpha)(n+A_2)(n+B_2)}{(1+\kappa)(n+C_2)(n+D_2)}X. \end{aligned}\right\} \quad . \quad . \quad . \quad (22')$$

The form of the factor n is determined by the initial condition. In this case there is one more unknown than condition, and there are two solutions, one of which is (22) and the other contains an arbitrary constant. This latter, however, reduces to (22) when $\alpha=-\frac{1}{2}$, and again when $\alpha\neq-\frac{1}{2}$ neither solution is physically significant. When $\alpha\neq-\frac{1}{2}$ we must therefore assume different forms for $b_{2n}{}^{\pm}$ and $b_{2n+1}{}^{\pm}$. These can be treated in the same way and solutions obtained, but it does not seem desirable to pursue such speculations further until experimental material is available.

§ 6. *Comparison with observation on visible bands.*—(i.) *Iodine Bands.* R. W. Wood's [*] observations on the fluorescent spectrum of I_2 vapour under stimulus by the Hg green line provide a delicate test of part of the foregoing theory (when there is no zero band), for atoms are present in a single initial state and emit the lines $(n)^+$ and $(n+1)^-$ with intensities proportional to $A_n{}^+$ and $A_{n+1}{}^-$. There are no statistical complications. The intensities emitted must therefore by (4) and (5) be proportional to $b_n{}^+$ and $b_{n+1}{}^-$. The analysis of these observations by Lenz [†] shows that n lies between 8 and 10. The ratio of the intensities should theoretically be

$$\frac{b_8{}^+}{b_9{}^-}=\frac{4}{5+\alpha},\quad \frac{b_9{}^+}{b_{10}{}^-}=\frac{5+\alpha}{5}\quad\text{or}\quad\frac{b_{10}{}^+}{b_{11}{}^-}=\frac{5}{6+\alpha}.\qquad(\alpha=0,\text{ or }-\tfrac{1}{2})$$

Wood states that under conditions free from subsequent reabsorption in the I_2 vapour all the pairs of fluorescent lines show equal intensities in every one of the 20 to 30 bands. The observations are probably in accord with theory for either value of α. The theory *might* demand a difference of as much as 10 per cent. in intensity in favour of the line of the negative branch (longer wave-length), which would scarcely have been recorded, as the lines do not appear to have been studied photometrically.

(ii.) *Other Emission Bands* [‡]. The experimental material available for discussion is as follows :—(A) An examination of intensities in the "Cyanogen band" λ 3883 by Birge*. He gives no details, but states that when $n^{\times}=30\cdot4$ the intensities in his spectrograms are well represented by the formula

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[*] R. W. Wood, Phil. Mag. xxxv. p. 236 (1918).

[†] Lenz, *Phys. Zeit.* xxi. p. 691 (1920).

[‡] I believe that I have followed Sommerfeld and Kratzer (Sommerfeld, *loc. cit.*) in calling "positive" that branch whose corresponding lines are of shorter wave-length. This branch is, however, frequently called R, or negative. Danger of confusion will be avoided if the definition "branch of shorter wave-lengths" is consistently borne in mind.

$$\alpha_n=c_1n^{3/2}e^{-c_2n^{3/2}},$$

from $n=5$ to $n=137$, if c_2 is adjusted to give the correct $n^{\times}$. The intensity curves of the two branches are similar in shape, but the branch of longer wave-lengths (Heulinger's P) is from 10 per cent. to 20 per cent. the more intense. The theoretical formula ($ne^{-c_3n^2}$) is stated to give the position of the maximum correctly, but to give intensities five times too small at the end of the band. This band is difficult for intensity work owing to the close spacing of the lines. The intensity difference in the two branches is confirmed by Schwan †.

(B) Intensities in the band-spectrum of copper (probably CuH) are recorded by Frerichs ‡. He gives intensity curves for the two branches of three bands with maxima at about $n^{\times}=13$, 14. The intensities of the early lines of the two branches in these bands are closely equal, and increase regularly and apparently linearly with n (not like $n^{3/2}$), but intensity differences develop towards the maxima, and thereafter the branch of longer wave-lengths (Frerichs' P) is uniformly the more intense. At the maxima the amounts as read from his figure 1 are 27 per cent., 13 per cent., and 11 per cent. Beyond the maxima the percentage difference seems to show a general tendency to go on increasing.

(C) Some intensities, which do not claim to be more than fragmentary, are recorded by Fassbender § for two of the negative Nitrogen bands (λ 3914, λ ?). The initial linear increase in intensity seems well shown and the approximate initial equality in the branches. Maxima occur at about $n^{\times}=10$, and the branch of longer wave-lengths is the more intense. The curves are not certain enough to give a quantitative intensity ratio.

To compare these results with the theory (for simplicity with $\alpha=-\frac{1}{2}$, $\epsilon=\frac{1}{2}$) we have *for emission*

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* Birge, *loc. cit.*

† M. Schwan, *Diss. Bonn* (1923). Not available for reference. Quoted by Frerichs, see below.

‡ Frerichs, *Zeit. für Phys.* xx. p. 170 (1923-4).

§ Fassbender, *Zeit. für Phys.* xxx. p. 73 (1924).

$$\alpha_n{}^{+}=\mathrm{X}n\,e^{-\delta(n+\frac{1}{2})^2/\mathrm{T}},\quad \alpha_n{}^{-}=\mathrm{X}n\,e^{-\delta(n-\frac{1}{2})^2/\mathrm{T}}, \quad . \quad (23)$$

$$\frac{\alpha_n{}^{-}}{\alpha_n{}^{+}}=e^{n/(n^{\times})^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

On the whole it appears as if the early lines have the proper sort of increase of intensity demanded by (10 or (13), but this conclusion must be tentative. On the other hand, the theory does definitely predict that the branch of *longer wave-length* should be the more intense *in emission* according to (24), and this is qualitatively in agreement with observation. For $n=n^{\times}=13\frac{1}{2}$, equation (24) gives $7\frac{1}{2}$ per cent. instead of the 27, 13, 11 per cent. recorded above. For Birge's Cyanogen band with $n^{\times}=30{\cdot}4$ it gives 3·3 per cent. at the maximum, rising to 15 per cent. at the end of the band (observed 10 per cent. to 20 per cent.). The shape of the observed and theoretical intensity curves would not be in good agreement, but much distortion is possible in emission bands purely from distortions of statistical equilibrium on which *the temperature factor* in (23) is based.

One can rest fairly content with the general agreement on existing data in the hope of confirmation or refutation to come, but one fundamental point must be made. *According to the present theory the branch of longer wave-lengths must be stronger in emission, the branch of shorter wave-lengths in absorption*, owing solely to statistical temperature factors. Both these requirements are confirmed by observation, if my interpretation of the infra-red absorptions is accepted, but this is admittedly doubtful and can be, and has been, questioned *. If one branch is to be the stronger both in emission and absorption, this can only be due to unequal values of $b_n{}^{+}$ and $b_n{}^{-}$. I believe that it would then have to be concluded that the structure given in § 2 must be radically altered. If one branch really is stronger in emission and the other in absorption, then this must primarily be a statistical temperature effect, and must be investigated as such. Points such as these, however, cannot be usefull discussed further at this stage.

§ 7. *Kratzer's doublet theory.*—Kratzer has proposed a theory of bands in which it is necessary to distinguish between positive and negative values of m. Corresponding positive and negative values form close doublets, except for the first line of each branch which is single. It is at present doubtful what field of validity (if any) this theory has, but it may be noticed that the intensity theory of this paper has an immediate application to such bands. Equations (10) continue to hold unaltered, but now all the $b_n\pm$ except $b_1\pm$ must be regarded as the sum $(b_n\pm)_1+(b_n\pm)_2$ of the contributions of Kratzer's doublet. The theory however gives in addition the ratios $(b_n\pm)_1/(b_n\pm)_2$, which must be practically unity except for small values of n. For small values they are slightly uncertain as they depend effectively on the precise distribution of the weight ϖ_m between the equal positive and negative values of m. A study of such doublet intensities might throw further light on Kratzer's theory, and perhaps on the weights themselves.

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* Frerichs, *loc. cit.* p. 178.

§ 8. *Summary.*—A general summary of the Correspondence Principle and its "refined" applications is given, with special reference to band-spectra. It is shown that the intensities of the lines in a single band must be expected to obey summation rules similar to those first recognized by Ornstein, Burger, and Dorgelo in atomic spectra. Precise formulæ for the relative intensities are given in terms of the weights for the lines of any band without a zero branch. With the help of particular molecular models the theory can probably be extended to include bands with zero branches. So far as the present rather meagre experimental data can take us, the theory seems to be in agreement with fact. It promises, when better experimental data are available, to provide direct evidence as to the weights of the states of a rotating molecule, and thus fill up an important gap in existing theory. It therefore suggests lines for fruitful experimental work.

In conclusion it is a pleasure to acknowledge the advantages I have derived from opportunities of discussion of these points with Prof. Bohr and Drs. Kramers and Heisenberg, and to tender my best thanks to the International Education Board for contributing so materially to these opportunities.

CXXIX. *The Significance of Spectroscopic Magneton Numbers.* *By* EDMUND C. STONER, *Ph.D.(Cambridge), Lecturer in Physics at the University of Leeds* *.

1. *Introduction.*

THE phenomena connected with the multiplet structure of spectral lines and the general Zeeman effect, while extraordinarily complicated, have been empirically coordinated in a very satisfactory and coherent manner by the work in particular of Landé and Sommerfeld. While assumed structures of the atom based on the usual quantum theory postulates have been of service in suggesting the kinds of relations to be anticipated, in detail it has proved impossible to deduce the experimentally correct relations as resulting from the properties which the atoms would naturally be supposed to possess. Independently of the fact that half quantum numbers have had to be introduced, the results have seemed to suggest that the ratio of the angular and magnetic atomic moments is by no means always the same, as required by classical quantum theory. To the core of the atom, for example, a double magnetic effect is ascribed. The experimental investigation of the gyromagnetic effect, moreover, has given some ground for the belief that these anomalies are fundamental; and this has led to the view that a basic alteration in the formulation of the quantum theory will be necessary before magneto-spectral atomic effects can be explained.

It seems, however, as though too complete a preoccupation with the complexity of the domain as a whole has rather obscured some of the strikingly "normal" features which emerge from a direct consideration of simpler particular cases. It is these which it is proposed to discuss here. Many of the results are inherent in the treatments of Landé and Sommerfeld; but while they there appear as special cases of anomaly, here they are obtained directly from a more straightforward and natural application of ordinary quantum ideas. In so far as this is possible, it suggests that the general phenomena may eventually be embodied in a scheme which is not purely artificial and formal.

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* Communicated by Prof. R. Whiddington, F.R.S.

An outline of the Landé-Sommerfeld systems of classification, and the method of coordination of results based on them, is first given (2), the results being discussed with reference to the formal physical model interpretations which have been used (3). It is shown that an assumption that has hitherto been made tacitly—that *mg* values correspond to magnetic moments—is justified (4). The simpler cases are then considered, leading to results which agree with what would be expected theoretically (5). These results are applied to the elucidation of the significance of the variation of spectral types across the periodic table (5); and core magnetic moments deduced are correlated with those obtained for ions in solution (6). After some general remarks concerning the occurrence of different relative orientations of the magnetic moments of a core and electron orbit (7), the question of angular momenta and the assignment of inner quantum numbers is briefly discussed (8). Finally the possibility of a magnetic interpretation of multiplet separations is considered, a qualitative explanation being given of the significance of "inverted" terms (9). The paper concludes with a summary (10).

2. *The Correlation of the Experimental Observations* *.

Spectral terms may be classified by assigning to them a total quantum number, n, an azimuthal number, k, and an inner quantum number, j. For $s, p, d \ldots$ terms, k has the values $1, 2, 3 \ldots$, and normally transitions only occur for which k changes by unity. When there is more than one energy level corresponding to a given nk, the terms are differentiated by the inner quantum numbers. In the assignment of these, there is a considerable amount of arbitrariness; but relative numbers may be given quite uniquely if it is assumed, as a fundamental postulate, that transitions only occur (normally) for which $\Delta j = 0$ or ± 1. The number r will be used to indicate the "permanent" term multiplicity ($r = 1, 2, 3 \ldots$ for singlets, doublets, triplets ...)—the terms with the smaller k's usually not having the full number of components. In the following table are given the j values assigned by Sommerfeld on this basis:—

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* For fuller details reference may be made to Sommerfeld: *Atombau und Spektrallinien*, Ch. 8 (4th Ed., 1924), and to Back and Landé: *Zeemaneffekt und Multiplettstruktur* (Springer, 1925). Probably the most important papers are:—Landé, *Zeit. für Phys.* xv. p. 189; xix. p. 112 (1923). Sommerfeld, *Ann. der Phys.* lxxiii. p. 209 (1924).

TABLE I.—j values (Sommerfeld).

Type of Term.	k \ r	1	3	5	2	4
s ………	1	0	1	2	$\frac{1}{2}$	$\frac{3}{2}$
p ………	2	1	2 1 0	3 2 1	$\frac{3}{2}$ $\frac{1}{2}$	$\frac{5}{2}$ $\frac{3}{2}$ $\frac{1}{2}$
d ………	3	2	3 2 1	4 3 2 1 0	$\frac{5}{2}$ $\frac{3}{2}$	$\frac{7}{2}$ $\frac{5}{2}$ $\frac{3}{2}$ $\frac{1}{2}$

The term components may then be distinguished by writing the inner quantum numbers as subscripts, triplet p terms being indicated by p_0, p_1, p_2. For even series, $\frac{1}{2}$ is added to the j value for convenience, giving p_1 and p_2 for the p doublet terms.

In a magnetic field each nkj term splits up into $2j+1$ equidistant components; and the separation of these from the original position expressed in wave numbers is given by

$$\Delta\nu = mg\Delta\nu_n. \quad \ldots\ldots \quad (1)$$

Here $\Delta\nu_n$ is the "normal" Larmor separation ($e\mathrm{H}/4\pi mc$), m the magnetic quantum number which takes the values $j, j-1, j-2, \ldots -j$ for each j term (and hence is integral for odd multiplets, and half-integral for even multiplets), and g the Landé "splitting factor" which may be written as

$$g = \frac{3}{2} + \frac{\left\{\frac{r}{2} - (k-\frac{1}{2})\right\}\left\{\frac{r}{2} + (k-\frac{1}{2})\right\}}{2j(j+1)}. \quad \ldots \quad (2)$$

The expression then covers completely the observations on the Zeeman effect in a weak magnetic field for ordinary spectra. (Second degree spectra of the neon type are more complicated and need not be considered at present.)

3. *Attempted Physical Interpretations.*

Several attempts have been made to interpret the formulæ by picture models of the atom. These differ in detail, but in general type they are similar; all present artificial and formal features, and indicate remarkable anomalies. Sommerfeld's treatment will be briefly outlined.

j is taken as the angular momentum of the atom as a whole (as a multiple of the unit $h/2\pi$), and is supposed to be the resultant of the vector addition of the moment of the core j_s, and that added by the series electron j_a, these being given by

$$j_s=\tfrac{1}{2}(r-1),\quad j_a=k-1,\quad r=2j_s+1. \quad . \quad . \quad (3)$$

Possible j values are then given by possible vector combinations of j_s and j_a giving values which are integral or half-integral according to j_s; the maximum and minimum values being

$$j_{\text{max.}}=j_s+j_a,\quad j_{\text{min.}}=|j_s-j_a|, \quad . \quad . \quad . \quad . \quad (4)$$

while for s terms it may be noted that $j=j_s$.

When a magnetic field is applied, m is taken as the resultant angular momentum in the direction of the field. If μ is the magnetic moment of the atom, then

$$m/j=\cos(\mu, \mathrm{H}). \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The change in energy of the configuration in the field is taken as

$$\Delta\mathrm{W}=\mu\mathrm{H}\cos(\mu, \mathrm{H}), \quad . \quad . \quad . \quad . \quad . \quad (6)$$

so that

$$\Delta\nu=\frac{1}{h}\,.\,\mu\mathrm{H}\,.\,\frac{m}{j},$$

or, expressing $\Delta\nu$ as a multiple of $\Delta\nu_n$, and μ and j as multiples of the Bohr units,

$$\Delta\nu=\frac{\mu}{j}\,.\,m. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If the ratio between the magnetic and angular moments was constant—that is if both possessed the theoretical values and μ was equal to j— then (7) would be equivalent to $\Delta\nu=m$. Actually $\Delta\nu=mg$, and therefore, on the basis of the above treatment,

$$g=\mu/j. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The splitting factor is therefore taken as giving the actual ratio of the magnetic to the angular moment of the atom, as opposed to the theoretical value 1.

Knowing the type of spectrum (and hence the value of r) to which an atom gives rise, it is clear that on the basis of the above equations, using the generalized and empirically correct value of g, the value for μ for an atom in any kj state may be determined, and also its component in the field direction. In particular, for s terms $\mu = 2j_s$, while the maximum μ is given by

$$\mu_{\max.} = 2j_s + j_a. \quad \ldots\ldots\ldots \quad (9)$$

In the attempts that have been made to deduce the g formula from the model (taking into account the j_s and j_a precessions about j), it has been taken as an empirical postulate that the core has a double magnetic effect. Working from this Sommerfeld, for example, deduces

$$g = \frac{\mu}{j} = 1 + \frac{j^2 + j_s^2 - j_a^2}{2j^2} \quad \ldots\ldots \quad (10)$$

This may be compared with the empirically correct expression which may be written in the form

$$g = 1 + \frac{j(j+1) + j_s(j_s+1) - j_a(j_a+1)}{2j(j+1)}. \quad \ldots \quad (11)$$

It will be seen that, even assuming the core anomaly, the result arrived at is incorrect; which is taken to indicate that two terms (j and $j+1$) must always be considered in deducing the splitting factor for one of them.

In a strong field the separations are always integral multiples of $\Delta\nu_n$, being given, in terms of this unit, following Pauli, by

$$\Delta\nu = \begin{Bmatrix} m + j - j_a & \text{for } m \geq j_s - j_a \\ 2m + j - j_s & \text{for } m \leq j_s - j_a \end{Bmatrix} \quad \ldots \quad (12)$$

An important generalization due to Pauli, which enables corresponding weak and strong mg values to be deduced, and which has been applied and extended by Landé, is the principle of the permanence of the g sums; Σg or Σmg taken over all the j's, for fixed values of r, k, and m, being the same for any field strength. The separations in a strong field, it should be noted, are measured not from each energy level, but from the "centre of gravity" of the whole set of j components of the nk term considered.

From a model point of view, the core and series electron may be supposed to orientate independently. The virtually direct experimental fact that the mg values are integral in itself suggests strongly that the assignment of half quantum numbers to the core and electron has little physical significance. In attempting to derive the formulæ, difficulties similar to those for weak fields are encountered; in particular it seems necessary to attribute double magnetic energy to the core.

4. *The Gerlach and Stern Experiments.*

In the methods of treatment which have been summarized above it has been tacitly assumed that the mg values give a measure of the magnetic moment, and not of the mechanical moment, of the atom in the field direction. Now the change in energy due to the Larmor precession may be written

$$\Delta W = \tfrac{1}{2}mr^2[(\omega+o)^2-\omega^2]$$
$$= mr^2\omega o, \quad \ldots \ldots \ldots \quad (13)$$

where $o=\frac{eH}{2mc}$. Writing $j'=mr^2\omega$ for the actual mechanical moment, and $\mu'=\frac{er^2\omega}{2c}$ for the corresponding magnetic moment,

$$\Delta W = j'o = \frac{mc}{2e}\mu' o. \quad \ldots \ldots \ldots \quad (14)$$

Using j and μ for the values as multiples of Bohr units, writing $\Delta W/h = \Delta\nu$, and expressing this in terms of $\Delta\nu_n(=o/2\pi)$,

$$\Delta\nu = j = \mu. \quad \ldots \ldots \ldots \quad (15)$$

$\Delta\nu$ is actually given by mg; but there is no *a priori* reason whatever for supposing that mg gives the magnetic rather than the angular moment, if these do not have their theoretical ratio.

The Gerlach and Stern experiments*, however, justify the assumption made; for in them the magnetic moment of atoms in the field direction is directly measured from the deflexion of a stream of atoms in a non-homogeneous magnetic field. For Ag, Cu, Au, $\mu=\pm 1$, corresponding to the normal s state with $mg=\pm 1$. For Zn, Cd, Hg $\mu=0$, corresponding to the singlet S state ($mg=0$). For Tl the separation is much smaller, and in approximate agreement with the value to be expected of the normal state is the p_1 with $mg=\pm 1/3$.

There is thus experimental evidence that the mg values do give the actual magnetic moments of the atoms. Now the j values cannot be found directly: they are assigned primarily in such a way as to provide a simple selection principle for allowable transitions ($\Delta j \not> 1$); and so may have no direct physical significance.

The gyromagnetic effect may be investigated by measuring the angular momentum of reaction due to magnetization of a (ferromagnetic) rod or wire. The ratio between the magnetic moment (M) and the angular moment (J) anticipated is

$$J/M = 2mc/e. \quad \ldots \ldots \ldots \quad (16)$$

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* *Ann. d. Phys.* lxxiv. p. 673 (1924); lxxvi. p. 163 (1925).

The ratio is found to be constant, and the directions are in agreement with the view that the elementary magnets consist of rotating electrons; but the value of the ratio is exactly half that expected, suggesting that for the atoms or units concerned

$$j = \tfrac{1}{2}\mu. \qquad \text{. . . . .} \qquad (17)$$

For atoms in an *s* state this would be anticipated, if Sommerfeld's formulation had definite physical significance; but there is no reason to suppose that the units concerned in Fe, Ni, Co, and Heusler alloys—all of which have been tried—should all be in an *s* state. Actually various values of the ratio, differing from each other, would be expected. At present the gyromagnetic anomaly can hardly be said to justify experimentally the artificial *j* schemes, or to be explained by them; the explanation is probably more straightforward. The anomaly is undoubtedly connected with the fact that atoms with definite magnetic moments exist, and orientation does occur (in accordance with the quantum theory), both of which do not allow of simple explanation on the classical theory.

5. *The Simple Cases.*

The simpler cases will now be considered, "simple" cases being taken as those in which, from a model point of view, the magnetic moments of the core and series electron are in the same direction, so that the resultant moment of the atom is obtained by the addition of the two constituent moments. For the atoms in the corresponding states, the moments in the field direction will be given by the *mg* values; and these, for the maximum values, are the same whether the core and electron are relatively strongly coupled (weak field) or independent (strong field).

The following table gives the maximum magnetic moments of the atoms in *s*, *p*, *d* states for different multiplicities.

TABLE II.—Maximum magnetic moments.

Multiplicity. r.		1	2	3	4	5	6	7
Term type.	s ($k=1$) ...	0	1	2	3	4	5	6
	p ($k=2$) ...	1	2	3	4	5	6	7
	d ($k=3$) ...	2	3	4	5	6	7	8

Now the natural supposition to make is that the magnetic moment of the series electron in a k orbit is actually given by k: a view which the table supports in that μ increases by 1 in passing from s to p to d terms. This assumption enables the magnetic moment of the core (μ_c) to be at once deduced, with the following result:—

Magnetic moment of core.

r	1	2	3	4	5
μ_c.....	-1	0	1	2	3

μ_c is in fact given by

$$\mu_c = r-2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

For an atom in any k state the maximum moment is given by

$$\mu_{\text{max.}} = \mu_c + k = r+k-2. \quad . \quad . \quad . \quad . \quad (19)$$

It is this simple and intelligible feature of the Zeeman effect which it is desired particularly to emphasize.

The deductions expressed in (18) and (19) fit in coherently with the known experimental facts, not only for atoms whose magnetic moments in the normal s state have been directly determined, but also for atom cores whose constitution is known. Doublets occur for Li, Na, K, etc., which consist of a series electron rotating round an inert gas core. Now the inert gases are diamagnetic, and of this the only natural interpretation is that they have no resultant magnetic moment. For Cu, Ag, Au the core, though not of the inert gas type, is a completed configuration in that the M, N, and O IV and V levels respectively are filled up *. Passing on to triplets (Mg, Ca, Sr, etc.) the core has a constitution similar to that of a doublet atom in the s state, so that $\mu_c=1$. If, however, the outermost core electron rotates in the opposite sense to the series electron, the maximum m_g values will all be smaller by 2, this corresponding to the singlet series.

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* The upbuilding of atoms is considered with reference to the scheme previously put forward for the distribution of electrons among atomic levels (Stoner, Phil. Mag. xlviii. p. 719, 1924), which has been discussed and developed by Sommerfeld, particularly in its spectroscopic bearings (*Phys. Zeit.* xxvi. p. 70, 1925). I have since found that the distribution had already been proposed, primarily on the basis of chemical arguments, by Main-Smith. (See 'Chemistry and Atomic Structure,' 1924.) It is very satisfactory that two different lines of attack should have led to the same conclusions.

It thus appears quite natural that an atom consisting of a series electron and a doublet s type core should give rise to singlet and triplet series

$$\begin{tikzcd} & r=3 & & \mu_c=1 \\ r=2 \arrow[ur] \arrow[dr] & & \text{corresponding to } \mu_c=0 \arrow[ur] \arrow[dr] & \\ & r=1 & & \mu_c=-1 \end{tikzcd}$$

In proceeding across the periodic table, three remarkable experimental facts emerge :—

I. The multiplicities are alternately odd and even.
II. The multiplicities corresponding to any atom are all odd or all even.
III. The maximum multiplicity observed corresponds to a value of μ_c which is not greater than the number of electrons the core contains in addition to those in the closed configuration with which the period begins.

This may be illustrated by the K–Ni period, for which the spectra have been most fully analysed.

Table III.—Observed Multiplicities.

(The most strongly developed are underlined.)

Element	K	Ca	Sc	Ti	V	Cr	Mn	Fe
Atomic Number Z...	19	20	21	22	23	24	25	26
Z−18−1	0	1	2	3	4	5	6	7
Observed Multiplicities.		$\underline{1}$		1				
	2		$\underline{2}$					
		3		$\underline{3}$				3
			4		$\underline{4}$		4	
				5		5		$\underline{5}$
					6		$\underline{6}$	
						$\underline{7}$		7
							8	

For other periods the details are less complete, but there is no disagreement observed with the rules given.

The results then suggest the rather surprising conclusion that the maximum contribution of a core electron to the magnetic moment of the core is 1; this would be expected for electrons added, for example, in s, or p_1 levels (that is in K, L, M, ... I or II levels), but not for those added in other levels for which $j > 1$.

This difficulty, however, partly arises from a too naive extrapolated application of the doublet level classification scheme to the whole process of upbuilding of atoms. That the scheme adopted * for completed configurations is the same as that which applies to doublet systems, rather than any other, has been regarded as somewhat formal and arbitrary; from the point of view of symmetry, however, it seems quite natural. In a doublet atom there is a completed core, and the series electron can occupy any of the levels constituting the next group; energy changes involve transitions of this one electron from any of the possible levels. In a completed configuration all the possible levels are occupied, and energy changes involve transitions of any of the electrons. When atoms are being built up by the gradual addition of electrons, the simple classification of orbits would no longer be expected to apply in its entirety. It is a matter for experiment to decide what scheme will work. The result is the Landé-Sommerfeld system for triplets and multiplets generally. These schemes apply to the atoms as wholes, and give a conspectus of the possible states they can assume. For the classification of orbits in "uncompleted" cores, however, there is as yet no direct evidence; it must be sought on the basis of the experimental rules given above, and by taking into account also phenomena connected with spectra showing different series of k terms with the same multiplicity (normal and "dashed" terms), corresponding to heteromorphic constitutions of the core.

From the observed regularities, it may be said that, for normal spectra, the addition of an electron to the core has the effect of increasing or decreasing its magnetic moment by unity. Further, the fact that atoms may give series with multiplicities differing by two, that is all odd or all even, is due, on the present view, as a first approximation, to a difference in the sense of rotation of one of the core electrons. Thus a core with three electrons in the outer incomplete group would have a magnetic moment of 3, 1, or -1 with $r = 5$, 3, or 1. In general it would appear that a core with

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* Stoner, *l. c.*

$2n$ outer electrons can have as possible magnetic moments 0, 2, 4 . . . . $2n$ (giving multiplicities 2, 4, 6 . . . . $2n+2$), and a core with $2n+1$ outer electrons -1, 1, 3 . . . . $2n+1$ (giving multiplicities 1, 3, 5 . . . . $2n+3$). The different core configurations will correspond to different energies and degrees of stability, and so all are not equally probable. Table III., for example, gives an indication of the magneton number of the core corresponding to the most stable configuration for the conditions under which the spectra are observed, namely, Ca -1, Sc 0, Ti 1, V 2, Cr 5, Mn 4, and Fe 3.

The possible multiplicities on this view depend solely on the number of "outer" electrons in the core, "outer" electrons being those the core possesses in addition to those forming a completed configuration. The maximum core magnetic moment is equal to this number, and the maximum multiplicity is greater by two. This statement covers both the displacement and branching rules * of Sommerfeld and Landé. It seems to apply not only to "normal" spectra, but also to those of the "second degree," for although the difficulties of the neon spectrum are formidable, in some ways it falls in simply with the above views. Of the 7 outer electrons of the core, the 3 more loosely bound form a secondary outermost group. Multiplicities of 5, 3, and 1, as observed, would be expected. The spectrum thus fits in coherently with the physically significant consequences of the unit magnetic moment idea.

6. *Ionic Magnetic Moments.*

It seems quite certain that not only atoms or molecules in gases, but also ions in solution tend to take up definite orientations which are determined by quantum conditions. Assuming orientation, the apparent Weiss magneton number (p) which would be deduced for an ion in solution, using the ordinary Langevin formula, corresponding to whole number Bohr magneton values, may be calculated. The results show that many ions may definitely be characterized by integral magnetic moments; and there are striking regularities in passing across the periodic table, the moment increasing from 0 to 5 in passing from an ion with 18 to one with 23 electrons, and then decreasing to zero for 28 electrons †.

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* Back and Landé, *l. c.* p. 55.

† *Atombau*, Ch. viii. p. 637 ff., or Sommerfeld, *Zeit. für Phys.* xix. p. 221 (1924).

(This corresponds to the filling up of the M IV and V sub-levels.) Both in this, and the rare earth group, however, there are anomalies, in that values departing considerably from those corresponding to whole numbers are frequently obtained. Sommerfeld[*] attributes this to the fact that the calculations are carried out on the assumption that the ions are in an *s* state, which (apart from the vagueness of the phrase applied to ions) is by no means necessarily true.

The considerations put forward above make it possible to correlate the spectroscopic and ionic moments in a very simple manner; and it seems worth while to do this, although some of the material is familiar.

An ion may be assumed to have approximately the same electronic configuration as an atomic core with the same number of electrons, provided that its resultant charge is the same. Now the fact that atoms can give rise to series with differing multiplicities indicates that the core can assume different magnetic moments; these are not necessarily equally stable, as is shown by the varying prominence of the series of different multiplicities (Table III.). So for an ion there may be different stable configurations; the most stable configuration need not be the same as that of the core with the same number of electrons, firstly because the nuclear charge is in general not the same, and secondly because temperature and other conditions may be widely different. Even if the ionic moments are all integral, there may be an equilibrium distribution between two or more types of ions resulting in apparent non-integral values.

The above remarks will probably serve as sufficient commentary to fig. 1, in which the circles give the possible core magnetic moments deduced as above from the spectra, the crosses the values obtained for ions in solution.

The ionic values[†] for which the crosses are drawn are given in Table IV., the subscript denoting the charge on the ion.

Particularly interesting is the case of V_2 and Cr_3; these ions have the same number of electrons, but the stable configurations correspond to different magneton values—very closely to 1 and 3. The fact that Co_2, Ni_2, and Cu_2 do not give whole number values suggests that an equilibrium is here concerned.

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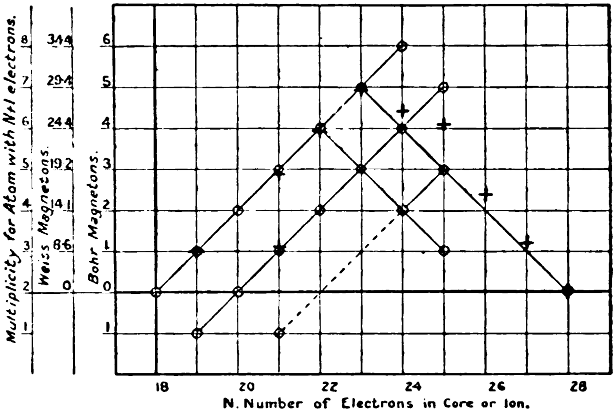
[*] *Atombau*, p. 644.

[†] The data are collected by Dorfmann, *Zeit. für Phys.* xxiii. p. 286 (1924). Papers by Cabrera, *Journ. de Phys.* iii. p. 443 (1922), and Weiss, *ibid.* v. p. 129 (1924), have also been consulted.

A corresponding figure for the rare earths is given. Most of the conclusions which can be drawn from it will be clear on inspection of the curves, and further discussion is of little value until more is known about the spectra. It is rather remarkable that Gd_3 ($N=61$), which has been most carefully investigated, with 7 electrons outside a closed configuration, has a magnetic moment very closely corresponding to 7 units (38·65 and 39·82 are values which have been obtained for p).

Fig. 1.—Magnetic Moments of Cores and Ions.



⊙ Magnetic moment of core from spectra.
+ Magnetic moment of ion from solution susceptibilities.

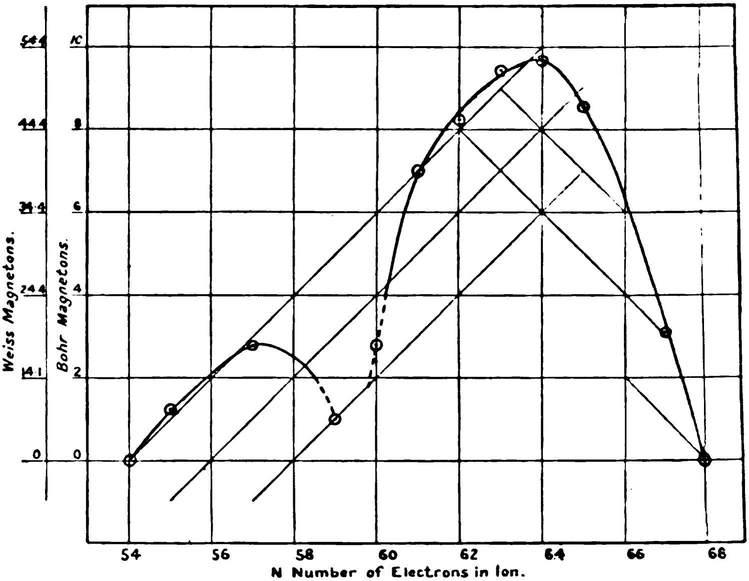
TABLE IV.—Ionic Moments.

(Expressed in terms of Weiss magnetons.)

N	18	19	20	21	22	23	24	25	26	27	28
Ion	Sc_3	Ti_3	...	V_2	Cr_2	Mn_2	Fe_2	Co_2	Ni_2	Cu_2	Cu_1
p	0	8·6	...	9·2	24	29·2	26·5	25	16	9·6	0
Ion	Ti_4	...	...	Cr_3	Mn_3	Fe_3	...	...	...	...	Zn_2
p	0	...	...	18·5	24·5	28·9	...	...	...	...	0

The straight lines are drawn to bring out clearly the relation of the observed ionic moments with those which might be anticipated, by analogy, for the cores. Since all the ions have the same resultant charge (3), the curve for the ionic moments suggests that the energy values of the N VI and N VII levels, which are being filled with 6 and 8 electrons respectively, are sufficiently far apart to reveal a double process of building up. In the A–Ni curve, however, there is no indication that two different levels (M IV and V) are involved *.

Fig. 2.—Rare Earth Ionic Moments.



The spectra of the rare earths undoubtedly offer an almost inexhaustible field for investigation. It may be noticed that from the ionic moments multiplicities as high as 12 may be anticipated.

7. *Some General Considerations.*

Except in the cases which have been considered, the magnetic moments of the core and orbit are not in the same direction; in the absence of a magnetic field they are orientated with respect to each other in a manner which must be governed by atomic symmetry demands, which are a consequence of the electric and magnetic properties of electrons rotating in orbits. The core and orbit can take up a discrete number of relative orientations, resulting in a discrete number of values for the magnetic moment of the atom as a whole. These are not necessarily integral. When a magnetic field is applied there are a discrete number of possible orientations of the atom as a whole in the field, the number again determined by the symmetry demands characteristic of the configuration involved. The resolved magnetic moments in the field direction are again not necessarily integral, as is proved by direct experiment.

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* *Cf.* Sommerfeld, *Ann. der Phys.* lxxvi. p. 290 (1925).

The attempt to force the phenomena into an artificial whole-number scheme seems merely to have added to the difficulties in understanding them. It must be remembered that the idea that the magnetic moment of an orbit in the field direction should be integral was rather a happy guess which enabled an idealized "normal" Zeeman effect to be explained on a quantum theory basis. The normal Zeeman effect observed for singlets involves a core and electron, both with magnetic moments, so that the mechanism concerned is much more complicated than a simple electron orbit. The actual phenomena seem better approached from an experimental standpoint rather than from a theoretical one which is based on a quite arbitrary, even if probable, hypothesis.

From the fact that the difference in energy value of the different magnetic components of a given kj term vanishes with the field, it must be supposed that the relative orientation of the core and orbit is the same for all of them. The triplet p_2 term, for example, in a magnetic field, is characterized by mg values -3, $-3/2$, 0, $+3/2$, $+3$; these must be regarded as giving the component of the magnetic moment, 3, in the field direction. For odd multiplicities the mg values are in the ratio 0, 1, 2 . . . ; for even multiplicities 1, 3, 5. . . . A direct interpretation is that the values give the directions of the magnetic axes with reference to the field; and that, in effect, a system of axes of symmetry characteristic of the state of the atom is revealed. As would be expected, there is a sharp distinction between the symmetry system characteristic of atoms with odd and those with even numbers of electrons.

Atoms with odd numbers of electrons do not give zero mg values; this is noteworthy, as it indicates that atoms with single unbalanced electron orbits do not set themselves with the plane of the orbit in the field direction—in agreement with the usual theory excluding such a setting in the simple case of the H atom, for example. When there are two electron orbits, however, as in singlet, triplet . . . systems, the zero mg value does occur, even for configurations with a resultant magnetic moment. It may be suggested that this indicates that the planes of the two orbits concerned do not pass through the nucleus. The whole of the Zeeman effect phenomena indicate the need for a fuller investigation of possible spatial atomic properties of a more far-reaching type than those that have previously been considered. Not only must orientation be taken into account, but also the possibility that the electron orbit planes do not pass through the nucleus.

Even when there is only a single electron associated with a completed diamagnetic core (simple doublet systems), the effects observed are quite different from those anticipated theoretically for a simple electron orbit. For the s term $mg = \pm 1$, and for p_2(max.) $mg = 2$; but considering all the magnetic components, the mg values for p_2 are ± 2, $\pm 2/3$, and for p_1 $\pm 1/3$. The electron orbit definitely does not set itself so as to give integral moments in the field direction—the presence of the core produces a modification, although it has itself no resultant magnetic moment. This might be attributed to several causes. The series electron might induce a diamagnetic moment in the core, with resultant reaction; this effect, however, would be small, and also would appear in the $mg_{\text{max.}}$ values. It must be remembered, however, that the core, though it has no resultant external moment, gives rise to strong local magnetic fields, and unless the series electron moves with respect to it in a perfectly symmetrical manner, it will show the influence of these fields. The mutual interaction resulting may be the fundamental reason for the observed divergences from integral values in the p_1 case, where the orbit and core have moments not in the same direction; but in the p_2 case there is no escape from the conclusion that there is no necessity for magnetic moments in the field direction to be integral; how far this applies to angular moments cannot at present be decided.

The above remarks are intended to bring out difficulties, in the belief that a clearer realization of them, in as close a relationship as possible to the actual experimental facts, may eventually lead to their being solved. A number of special points will now be briefly discussed.

8. *Inner Quantum Numbers.*

As has been pointed out, the inner quantum numbers are at present assigned in such a way as to enable a more or less arbitrary selection principle for possible transitions to be satisfied. Although it is quite reasonable to suppose that the j's so assigned are closely related to the angular moments of the atoms as wholes, there is little justification for interpreting the j's as giving these directly, unless this leads to a satisfactory physical "model." The Landé, Sommerfeld, and Bohr j values are different. Hicks [*] has recently pointed out that by adopting a selection principle $j \longrightarrow j+2,\ \ j,\ \ j-2$, and starting from $j=0$ and 1 for odd and even multiplicities, a scheme is obtained which is equally satisfactory; it avoids half-integral j values, and leads to comparatively simple expressions for the splitting factor g.

The angular moment of the atom as a whole, provided it is controlled mainly by the moments of the electrons, should be equal, in the appropriate units, to the magnetic moment; but it cannot be determined directly. Moreover, at present the correct mode of applying theory is too much in doubt to enable the ratios of the magnetic and angular moments of the individual atoms to be deduced from observations on the gyromagnetic effect. The difficulty of the gyromagnetic anomaly must be cleared up before much further progress can be made.

The gyromagnetic effect, however, does certainly suggest that for ions and cores $j=\frac{1}{2}\mu$; for this reason the classification of Landé, which is equivalent to putting $j_{\text{max.}} = \frac{1}{2}\mu_c + k$, using the core values arrived at above, with other values accordingly, has probably the closest relation to reality; moreover, it has the convenience of simplicity, for the term multiplicities, or statistical weights, are then given by $2j$. The physical fact is that only certain transitions occur; but arbitrary j schemes will do little to explain this.

9. *Interval Relations and Inverted Terms.*

Landé has deduced that the intervals between terms of a multiplet should be in the ratio 1 : 2 : 3 . . . for odd, and 3 : 5 : 7 . . . for even multiplicities. This holds closely in a number of cases, but the data collected by Hicks [†] show that in general the agreement is poor, the ratios only serving to give the relative order of magnitude of the intervals.

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[*] Hicks, Phil. Mag. xlviii. p. 1036 (1924).

[†] Hicks, *l. c.*

The relation is deduced on a formal model basis, by attributing to the core and series electron mutual magnetic energy of amount $\mu_c \mu_e \cos \theta$, θ being the angle between the moments; the relative intervals can then be deduced, $\cos \theta$ being derived, again formally, from the constituent j's involved. The magnetic theory is unable to account satisfactorily for the absolute intervals, these, as is well known, being given very closely by the Sommerfeld relativity formula with an appropriate, admittedly formal, choice of k's *. The treatment of electron orbits and cores virtually as magnetic shells is, however, very crude, and a closer consideration of the processes involved seems to throw light on some of the difficulties, particularly in connexion with "inverted" terms.

In most of the spectra which have been analysed, the kj components with the highest values of j correspond to the orbits in which the electrons are most loosely bound to the nucleus, the negative energies being smaller. This may be expressed by

$$\overset{r}{n}_{kj} < \overset{r}{n}_{k,j-1} .$$

For inverted terms, on the other hand,

$$\overset{r}{n}_{k,j} > \overset{r}{n}_{k,j-1} .$$

As an example in the Mn sextet system all the D and F terms are inverted. No satisfactory explanation of these inverted terms seems to have been given, though Sommerfeld has pointed out that they occur when the ground term would be a p_2 term, as in N, P, etc.†

Consider a simple idealized case in which the core consists of a nucleus with a single electron going round it. A series electron will suffer magnetic perturbation as it passes through the field of the core. The perturbations will be greatest where the electron is moving with its greatest velocity in regions where the field is strong. For elliptical orbits in general, the energy changes arising from the magnetic perturbations, which control the interval relations, will thus depend mainly on the inner parts of the orbits. The energy corresponding to orbits of different orientations, moreover, will change progressively owing to the change in the field through which the electron passes; but whether the change the electron orbit depends on the extent to which the electron will correspond to an increase or a decrease in the energy of

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* Landé, *Zeit. für Phys.* xxiv. p. 88; xxv. p. 46 (1924).

† Sommerfeld, *Phys. Zeit.* xxvi. p. 70 (1925).

penetrates the core; for the field due to the core electron has a different direction inside and outside its orbit.

For complicated cores the details would be exceedingly difficult to work out; but the above considerations may be expected to apply in a general way, and terms may be expected to be normal or inverted according to the extent to which the series electron orbits concerned penetrate the core, or the effective magnetic part of it. If they only penetrate to regions where the field is inverted, the terms will be inverted. Actually the orbit generally passes through both normal and inverted parts of the core field, and the resultant energy change depends on which produces the greater effect, the predominating influence usually being that due to the field where the series electron is moving closest to the nucleus.

The observations may now be considered *. First it may be noted that definitely penetrating orbits give rise to normal terms; and that inverted terms tend to appear for higher azimuthal quantum number orbits ($d, f\ldots$), and for a given k for higher values of n (corresponding to a relatively greater non-penetrating portion of the orbit). Among the alkali metals, K d terms are probably inverted, with small intervals; Cs d terms are normal, but f terms are inverted. Na d terms are doubtful, but the corresponding Mg II and Al III d terms are inverted. Ca II d terms, and Ba II f terms are normal. It would appear that for similar electron configurations, the higher the nuclear charge, or the higher the resultant core charge, the more persistent is the tendency to "normality"; the extent of penetration roughly corresponds. Li p and d terms, also B III p terms are all normal. This is true also of the p terms of Al, Ga, In, Tl.

At the other end of the periodic table where the cores are smaller, owing to the higher nuclear charge, and where the series electron can be sharply differentiated from the core electrons, inverted terms become much more prominent. Practically all the Fe terms are inverted. The quintet g group is interesting in that $g_2 \ldots g_5$ are inverted, $g_5\ g_6$ normal. The main effect on the g_5, g_6 orbits presumably occurs where the electron traverses a normal region of the core field. The Mn octet terms appear to be normal, but the sextet D and F terms are all inverted, as also the P terms with the exception of the first two members. The possibilities of inversion are to be expected in this case, for the sextet core ($\mu_c = 4$) has less than its maximum moment,

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* The data are collected in Sommerfeld, *Atombau*, p. 685 ff.

owing to the balancing of the magnetic effects of core electron orbits. This will give rise to marked local inverse fields.

With the data available further discussion would be of little value. It seems probable, however, that on the lines sketched out it may be possible to link normal and inverted terms into a single and coherent scheme. "Correct" normal and inverted intervals are of course limiting cases; in between, "anomalous" intervals will occur. The question is connected with that of term magnitudes in general, and in particular with the anomalies occurring in the intervals in passing from lower to higher members of a given series, such as the *f* series of BaI *, investigated by Saunders. On the whole it seems that the incompleteness in the magnetic explanations of many presumably magnetic spectral effects is due to the extreme difficulties confronting attempts at precise mathematical calculation, rather than to fundamental inconsistencies in the theory itself.

10. *Summary.*

A brief outline is given of the Landé-Sommerfeld schemes coordinating observations on the multiplet structure of spectral lines and their Zeeman effect. The artificial and anomalous features in the attempted physical interpretations are pointed out.

Simple cases are then considered. From these it is concluded that electron orbits and cores are characterized by integral magnetic moments (in terms of the Bohr unit). The magnetic moment of an electron orbit is given by its azimuthal quantum number. The maximum magnetic moment of a core is equal to the number of electrons it contains in uncompleted groups. This determines the maximum term multiplicity (2 greater than the core moment). Magnetic balancing in pairs of core electrons gives rise to lower multiplicities, all odd or all even for odd or even numbers of core electrons.

The magnetic moments deduced spectroscopically are in agreement with those found directly in the Gerlach and Stern experiments, and the core values are simply correlated with the ionic moments deduced from susceptibility measurements.

The question of angular moments, and the assignment of *j* values is discussed.

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* *Atombau*, p. 690.

Finally it is shown that a consideration of the motion of the series electron in the magnetic field of the core leads to a general qualitative explanation of the physical significance of inverted terms, and interval anomalies.

April, 1925.

Note added to proof.—In a recent paper on the connexion between the completing of electron groups in atoms with the multiplet structure of spectra, Pauli has discussed in detail, with important conclusions, several questions closely related to those here considered, particularly in section 5. Pauli, *Zeit. für Phys.* xxxi. p. 765 (1925).

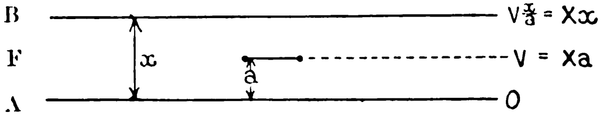
CXXX. *Electrical Properties of Neon, Hydrogen, and Nitrogen.*

By S. P. McCallum, *B.A.*, *Hertford College*, *and* C. M. Focken, *Rhodes Scholar*, *Lincoln College*, *Oxford*[*].

1. In a recent paper[†] J. S. Townsend and S. P. McCallum describe an investigation of some of the electrical properties of helium by a new method. This investigation was undertaken primarily to decide by a direct experiment whether there was any appreciable effect due to radiation, comparable with the effect of ionization by collision, during the earlier stages of the development of large currents in gases, and whether the rate of increase of current with increase of potential between the electrodes was the same where the source of electrons was a heated filament and where the electrons were produced by ultra-violet light falling on a silvered plate. This paper describes further investigations with the same apparatus on neon, hydrogen, and nitrogen.

2. A detailed description of the apparatus was given in the paper already mentioned, and we give here only such details as are essential for the understanding of the method used. This involves the measurement of the currents to two silvered plate electrodes A and B (fig. 1).

Fig. 1.



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[*] Communicated by Prof. J. S. Townsend, F.R.S.

[†] Phil. Mag. xlvii. (April 1924).

A short filament F of fine platinum wire was supported by two silver wires between A and B at a fixed distance a from the lower plate A. The upper plate B was mounted on an axle with a micrometer so that it was capable of adjustment at any distance x from the plate A between 10 and 18 millimetres. A, B, and F were accurately parallel, and the distance a of F from A was 7 millimetres. In each experiment the lower plate A was kept at zero potential; the filament F was maintained at a negative potential V; the upper plate B was maintained at the negative potential $V\frac{x}{a}$. This establishes a uniform field $X=\frac{V}{a}$ between the plates except near the filament and its supporting wires. It is important to notice that, when the distance x is changed from x_1 to x_2 and the potential of B from Xx_1 to Xx_2, there will be no appreciable change in the distribution of the electric force in the space near the filament F and its supporting wires.

The upper plate B was usually adjusted in the experiments at three different distances, and for convenience the distance x was made a simple multiple of the distance a, e.g., $x_1=1{\cdot}5a$; $x_2=2a$; $x_3=2{\cdot}5a$. By means of a potentiometer the ratios of the potential of the upper plate B to the filament F could be adjusted very accurately; this is very necessary in determining current-potential curves, as the emission current from a filament is very sensitive to changes in the distribution of the field around it. The filament was heated to a dull red by a battery of large accumulators, and small emission currents of the order of 10^{-12} to 10^{-11} ampere were used, in order to avoid the disturbing effects of large numbers of electrons or positive ions in the field between the plates. With the small currents used the relative values of the currents for different forces were independent of the filament emission. The fall of potential down the filament was about a quarter of a volt, but no appreciable error is made in these experiments by taking the potential of the filament as V.

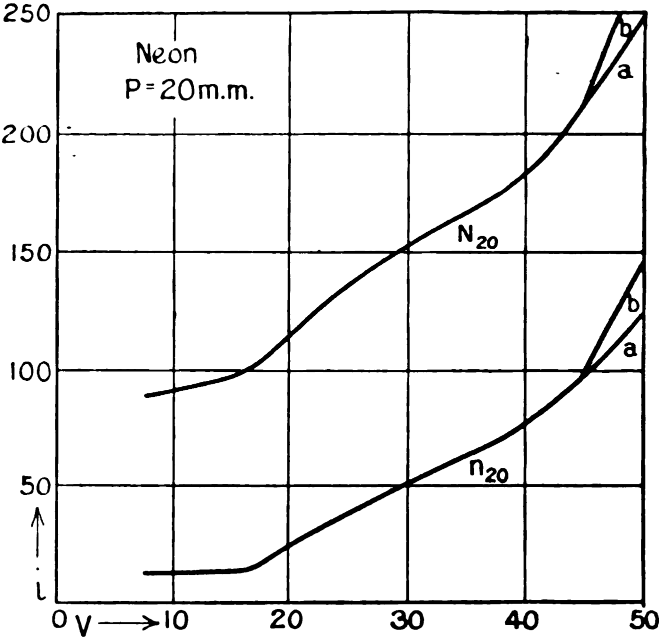
An induction balance, using a sensitive electrometer as indicator, was used to measure the currents to the plates, and it was arranged so that the ratio of the currents to both the plates could be measured over the same interval of time. This ratio would then be independent of the filament emission, and could be used to check the ratio of the ordinates representing the currents to the two plates obtained with a constant filament emission.

3. The following method was adopted in carrying out the

experiments :—The filament was thoroughly glowed out and heated for several hours until the emission had become constant and the positive ions ceased to be emitted. The gas in the apparatus was then pumped out quickly and flushed out with samples of pure gas. A fresh sample at the required pressure was then admitted on which the experiments on conductivity were made. The upper plate B was then set at the distance x, and the potentials of the filament and the upper plate adjusted to V and $V\frac{x}{a}$ respectively. Measurements were then made of the negative currents to the plate A and the positive currents to the plate B for the different values of V. The ratios of the positive and negative currents, obtained during the same intervals of time, were also measured by the induction balance for the different values of V, and the determinations were used to check the ratios of the ordinates of the current-electromotive force curves. The results of these two methods were in very good agreement. The upper plate B was then set at another distance x_2, and the potential of B was adjusted to $V\frac{x_2}{a}$. The negative and positive currents for this distance were then measured for the same values of V as were used for the distance x_1 and for the same filament emission. The results of the experiments are given in the form of current-potential curves in which the ordinates represent the currents in arbitrary units and the abscissæ the potential in volts between the filament and the lower plate A, this being the potential through which the electrons, emitted from the filament, fall in passing to the plate A. The curves show the ratio of the positive current to the negative current for each distance x and potential V.

The curves given in fig. 2 represent the results of the experiments with neon at 20 millimetres pressure. Curve N_{20} gives the negative currents to the plate A, and curve n_{20} the positive current to the plate B. The experiments were made with two different distances between the plates $x_1 = 12$ mm. and $x_2 = 17{\cdot}5$ mm. The currents were exactly the same for the two distances, for the smaller potentials of the filament up to 45 volts. For larger potentials from $V = 45$ to $V = 50$ the currents obtained with the larger distance x_2 were greater than those obtained with the smaller distance x_1. In fig. 2 the branches of the curves marked *a* correspond to the distance $x_1 = 12$ mm., and those marked *b* to the distance $x_2 = 17{\cdot}5$ mm. This increase in the currents with the increase of the distance corresponds to the effect observed in experiments on photo-electric currents where the rate of increase of the current with the distance between the plates exceeds the rate of increase of the quantity $A\epsilon^{\alpha x}$. As was pointed out in the previous paper, the results of the experiments are completely different from what would be expected if the electrons, emitted from the filament, were capable of exciting radiation in their collisions with the molecules of the gas, which would set free an appreciable number of electrons from

Fig. 2.



the upper plate B. If the increase in the current with potential be due to photo-electric emission from the upper plate B, it is possible to calculate approximately the effect at the two different distances. Thus at the point V=35 volts, when x is changed from 12 mm. to 17·5 mm. electrons from the upper plate would have their paths increased in traversing the distance between the plates with an increase of potential along the path of 27·5 volts. The current to the upper plate when $x=17{\cdot}5$ mm. would then be about twice the current with the distance $x=12$ mm. But as no difference was observed between these currents, it is evident that any effect due to radiation must be small compared with the principal effect to which the increase of the current must be attributed. Also, on the radiation hypothesis a large continuous discharge should take place with the plates at 17·5 mm. apart when the potential V is about 50 volts; but no such effect was obtained.

Further, it can be shown that at the higher potentials, when the currents between the plates are increased by increasing the distance between the plates, the additional process of ionization rises in importance as X/p increases in the same way as the values of the current i exceed the quantity $A\epsilon^{\alpha x}$ in the experiments with photo-electric currents. This is in accordance with the effect which would result from the ionization of the molecules of the gas by the impact of positive ions or from electrons set free from the negative electrode by the impacts of positive ions, but is not in accordance with the assumption that the effect is due to electrons set free from the negative electrode by radiation from the molecules of the gas.

The neon used in the experiments was very carefully purified by means of charcoal maintained at the temperature of liquid air for about 12 hours. As it was found that the gas was sensitive to traces of impurity, a tube containing charcoal was connected to the apparatus and maintained at the temperature of liquid air during the experiments. The experiments were carried out as soon as possible after fresh gas was admitted to the apparatus, so as to avoid the effect of impurities emanating from the surface of the metal case of the instrument.

A set of curves is shown in fig. 3 for neon at 7 millimetres pressure for two different distances between the plates 12 mm. and 17·5 mm. These curves, the positives being distinguished by the letter n_7 and the negatives by the letter N_7, coincide up to the point where V is 42 volts, but above that voltage the currents for the larger distance 17·5 mm. are greater than those for the smaller distance 12 mm., the branches being marked b and a respectively.

In the table given below are shown the values of the potential for different pressures at which the curves show appreciable divergence, that is the point at which some process of ionization becomes appreciable, in addition to the ionization by collision of electrons with the molecules of the gas.

Fig. 3.

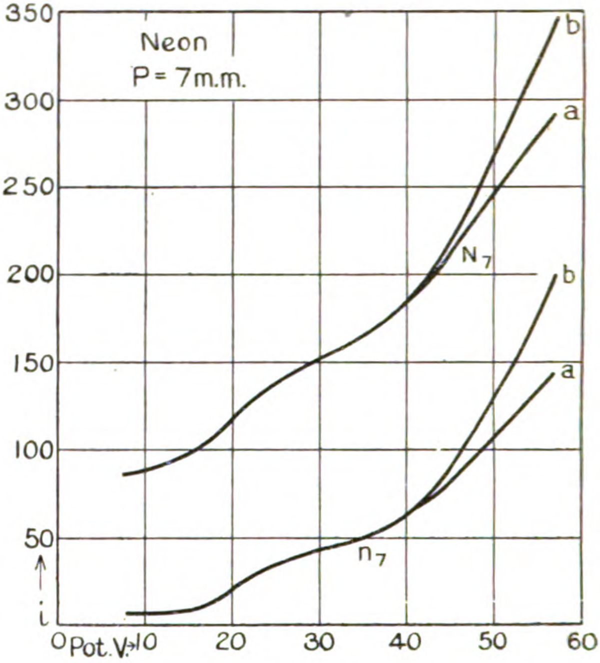


TABLE I.

p in mm.	V filament potential.	$\frac{X}{p}$.	Potential between plates $V\frac{x}{a}$ ($x=17\cdot5$ mm.).
20	45 volts.	3·2	113 volts.
7	42 ,,	8·6	105 ,,
2·5	40 ,,	22·9	100 ,,

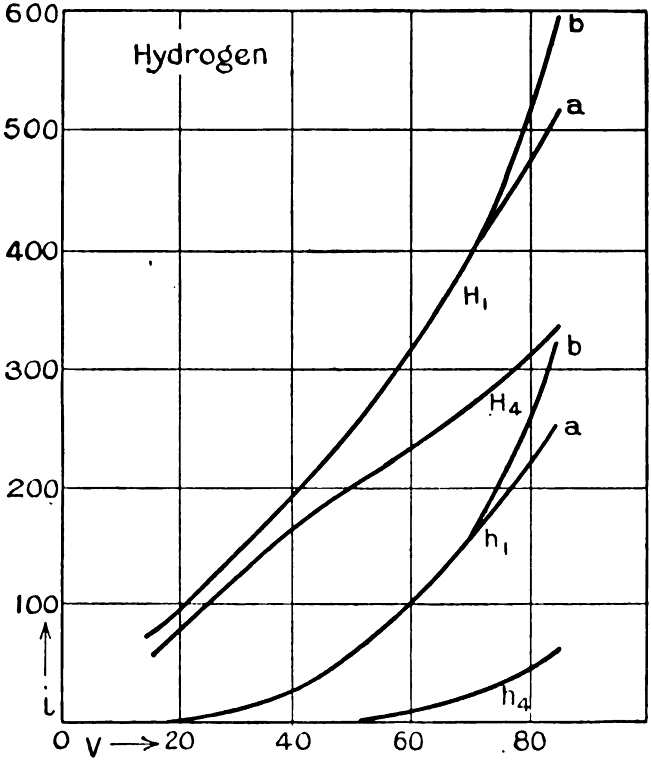
No accurate experiments have as yet been published on the photo-electric currents between parallel plates in neon, but some preliminary experiments we have made show that an additional process of ionization becomes appreciable when $X/p=5\cdot5$ at about 115 volts, and when $X/p=15$ at about 105 volts.

5. Experiments were also made with hydrogen. It was obtained by electrolysis of barium hydrate, and passed through a heated palladium tube into the apparatus. Before

each experiment, pure gas was passed through the apparatus and pumped out so as to remove any impurities which may have been present during the glowing-out of the filament.

The curves in fig. 4 represent some of the results for hydrogen. Curves H_4 and h_4 show the value of the negative and positive currents to the electrodes A and B respectively in the gas at 4 mm. pressure for different values of V up to 85 volts. Similarly, the curves H_1 and h_1 represent the results for hydrogen at 1 mm. pressure. With the pressure of 4 mm. the curves obtained for the different values of the distance x from 10·5 mm. to 17 mm. coincided up to the highest value of the potential used, *i. e.* V=85 volts, which corresponds when $x=17\cdot5$ mm. to a potential difference between the plates of 212·5 volts and a value of X/p of 30·4. At a pressure of 1 mm. a divergence between the currents was obtained in changing the distance between the plates from 10·5 mm. to 17·5 mm. It became appreciable when

Fig. 4.



$V=72$ volts, which corresponds to a potential difference between the plates of 180 volts for the largest distance of 17·5 mm. and the value of X/p is 103. The curves giving the positive and negative currents with hydrogen at 1 mm. pressure for the two different distances between the plates of 10·5 mm. and 17·5 mm. are distinguished where they diverge by the letters *a* and *b* as in the curves for neon. At a pressure of ·53 mm. the divergence between the curves occurred at a lower filament potential, $V=60$ volts, than at the pressure 1 mm. The points at which an additional process of ionization becomes appreciable is shown in Table II.

TABLE II.

p in mm.	V filament potential.	$\frac{X}{p}$.	Potential between plates V_a^x ($x=17·5$ mm.).
1	72 volts.	103	180 volts.
·53	60 ,,	163	150 ,,

From determinations of the number of ions generated by collision in hydrogen * we have calculated that the current i between parallel plates first exceeds the quantity Ae^{ax} by an appreciable amount, when the potential difference between the plates is 200 volts for $X/p=88$ and 140 volts for $X/p=175$. These values are in good agreement with those shown in Table II.

6. Some experiments were also made with nitrogen. We are indebted to Mr. Lambert for providing us with a very carefully prepared sample of the gas.

In fig. 5 are shown the curves obtained with two of the pressures used, viz. ·15 mm. and 1·2 mm. $r_{·15}$ and $R_{·15}$ represent the values of the positive and negative currents in the gas at ·15 mm. pressure, while the letters *a* and *b* distinguish the curves (after they diverge) obtained for the currents at the two different values of x of 10·5 mm. and 17·5 mm. It will be noticed from the curves for the pressure 1·2 mm. that no additional process of ionization becomes appreciable for the values of the potential used, *i.e.* up to 185 volts between the plates; but for the pressure ·15 mm. the curves show a divergence when $V=46$ volts, $X/p=438$, and the potential difference between the plates is 115 volts. From experiments † on ionization by collision between parallel plates in nitrogen we have calculated that i first exceeds the quantity $A\epsilon^{\alpha x}$ by an appreciable amount when the difference of potential between the plates is 120 volts for $X/p=350$ and 105 volts when $X/p=525$. Here again the results show good agreement.

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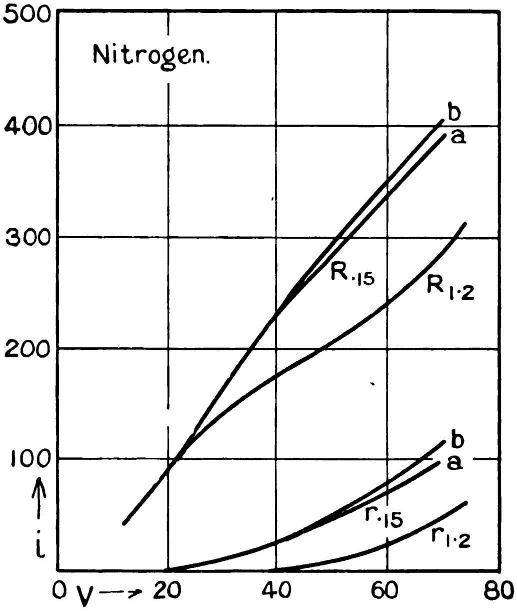
* J. S. Townsend, Phil. Mag. Nov. 1903.

† H. E. Hurst, Phil. Mag. xi. p. 535 (1906).

Fig. 5.

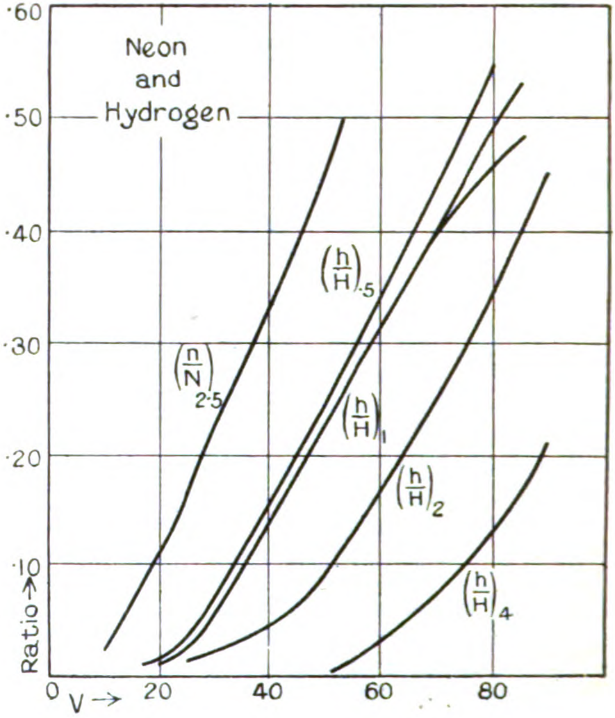


7. In figs. 6 and 7 are plotted the ratios of the positive current to the plate B to the negative current to the plate A for the three gases at different pressures. For example, the curves in figs. 6 and 7 are denoted; in the case of hydrogen at 1 mm. pressure by $\left(\frac{h}{H}\right)_1$, the ordinate at any point giving the ratio of the positive current to the negative current, while the abscissa gives the potential between the filament and the lower plate. Similarly, the curves for neon at 2·5 mm. pressure and nitrogen at 1·2 mm. pressure are denoted respectively by $\left(\frac{n}{N}\right)_{2\cdot5}$ and $\left(\frac{r}{R}\right)_{1\cdot2}$. In order not to complicate the figures, the effect of increasing the

distance between the plates for the higher values of V is shown only in the case of $\left(\frac{r}{R}\right)_{\cdot 15}$ and $\left(\frac{h}{H}\right)_{1}$.

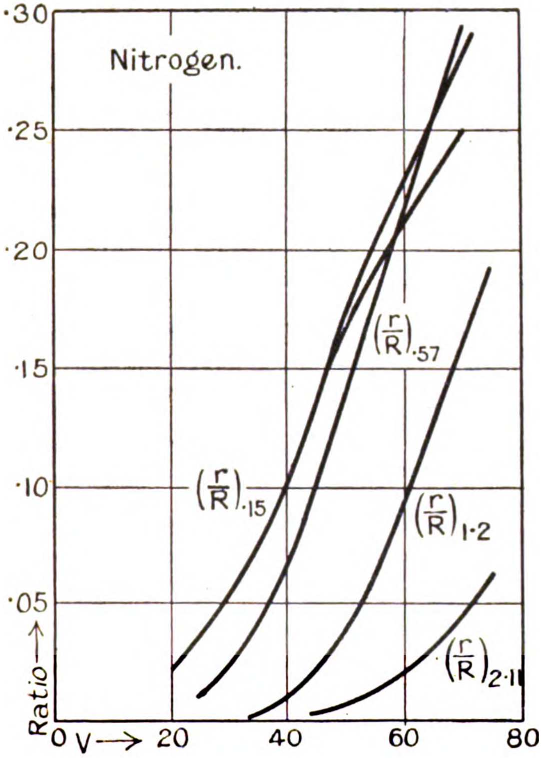
It will be seen from the curves in figs. 6 and 7 that the rate of increase of ionization with increase in electric force $(X=V/a)$ is very much greater in neon than in the two diatomic gases hydrogen and nitrogen. Further, in neon as in helium there is only a very small change in the rate of increase of ionization with electric force for large changes of pressure (for example, from 2 mm. to 20 mm. pressure), whereas in the diatomic gases increases from 1 mm. to 4 mm. in hydrogen and from ·5 mm. to 2 mm. in nitrogen produce large changes in the electrical conductivity. This is the result to be expected if the electrons lose large amounts of energy in collisions which do not produce ionization, which is in accordance with the results of

Fig. 6.



other experiments made in this laboratory on the loss of energy of electrons in collision with the molecules of gases.

Fig. 7.



8. The investigation does not indicate the exact cause of the additional ionization which becomes appreciable for the higher values of the electric force, except that it cannot be attributed to the photo-electric action of radiation of a type which has been suggested. Since the effect of the additional process of ionization increases continuously with the ratio X/p, it appears to be due to positive ions which become more active as their velocity increases, or to radiation excited by collisions of electrons when moving with velocities much greater than that required to ionize the molecules of the gas. The experiments show that this action is much larger in monatomic gases than in diatomic gases. In helium it is

appreciable in currents between parallel plates when the potential difference is 108 volts and X/p is 30, and in neon for a potential difference of 105 volts when X/p is 15. But in hydrogen the effect does not become appreciable until the potential difference between the plates is 200 volts and X/p is 88, while in nitrogen it takes place at 210 volts when the ratio X/p is 130. It is probable, then, that the action is due to positive ions, which should lose less energy in collisions which do not produce ionization in monatomic gases than in diatomic gases while falling through the same electric force.

9. The authors wish to thank Professor Townsend for his unfailing interest in the experiments and his ever-ready help and advice.

CXXXI. *Semi-optical Lines in the X-ray Spectra.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the April issue of the Phil. Mag. Messrs. A. Dauvillier and L. de Broglie draw attention to some previous investigations by themselves *, where some of the results given in our paper † are said to be obtained. It seems to us that the ideas underlying their paper are so fundamentally different from ours that there was no reason for giving the reference. Messrs. Dauvillier and de Broglie operate with a system of 6 M and 10 N levels, whereas our conclusions refer to the generally-accepted number of levels, 5 M and 7 N, and to the distribution of the electrons among those levels as given by Stoner ‡.

It is, however, interesting to note that Messrs. Dauvillier and de Broglie also, on the basis of their system, find it possible to explain the experimental results given in the diagrams (figs. 1 and 2) of our paper.

Yours sincerely,
E. BÄCKLIN,
M. SIEGBAHN,
R. THORÆUS.

Upsala, Physical Laboratory,
May 5, 1925.

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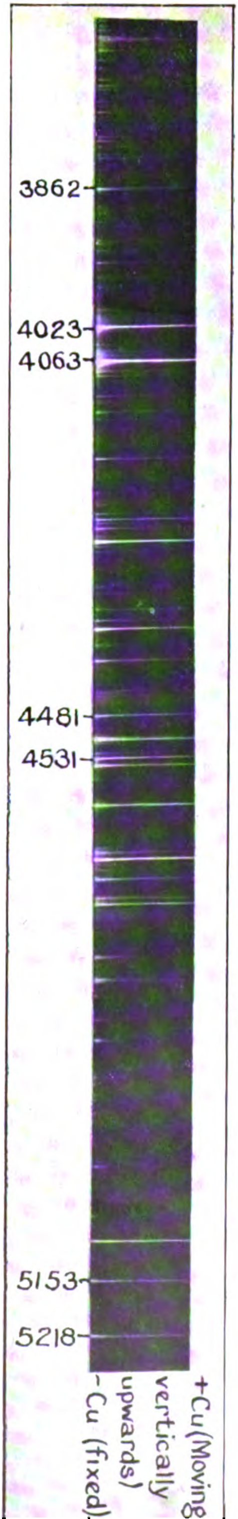
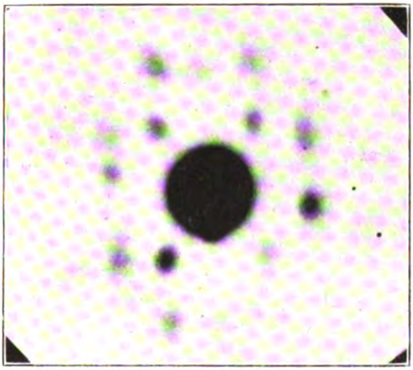
* *Journal de Physique et le Radium*, Jan. 1924.
† Phil. Mag. Feb. 1925.
‡ Phil. Mag. Oct. 1924.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]



Interrupted Arc Spectrum of Copper.



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